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TREATMENT OF PITCH WITH METHANOL

FINAL REPORT

for

ENERGY, MINES AND RESOURCES CANADA

Scientific Authority:

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PREFACE

Pitch with a boiling point above 525°C, is a heavy residue from refining/upgrading processes. Because of its high content of sulfur and metals, pitch cannot meet the Canadian combustion specifications, and is not suitable as a starting material for making electrode coke.

As demand for transportation fuels intensifies and the reserves of light crude diminish, hydrocracking processes will be increasingly utilized to upgrade bitumen and heavy oils. As a result it is expected that a considerable amount of pitch will be produced. The storing or disposal of the pitch has been identified as one of the problems in future operations.

As part of the effort to establish new technologies for conversion of the pitch into marketable liquids, CANMET initiated in 1984 a research program for use of methanol for upgrading of the 525° - C pitch into distillable products.

Sandwell Technologies was awarded a research contract for preliminary work using autoclave reactors in batch mode. The objectives of this program were to investigate the applicability of the pitch upgrading with methanol concept, conduct catalyst screening and study the effect of reaction parameters upon the pitch conversion.

The present report contains a description of the work carried out, the results obtained and the conclusions of the testing program.

The Scientific Authority during the first 10 months of the contract was Dr. M.A. Poirer and after his leaving CANMET, the Scientific Authority was changed to Dr. David P.C. Fung.

Santech would like to acknowledge Dr. R.B. Anderson's contribution to this work and to express its gratitude and appreciation for the excelency of his advise.

Summary

Sandwell Technologies was awarded the contract to carry out preliminary testing using its batch hot-charge reactor on the upgrading of pitch with methanol. This new concept originated by CANMET involves producing distillates from vacuum residues by hydrocracking in presence of methanol as hydrogen donor.

The testing program undertaken by Sandtech covered the selection of suitable catalysts and of reaction parameters, as well as the investigation of the effect of these parameters over the pitch conversion.

This report describes the equipment used, the procedures developed for the testing, the main experimental results, some preliminary economic considerations and the conclusions drawn at the completion of research.

Santech carried out 24 tests using a 525°C - pitch supplied by CANMET and technical grade methanol. Only the tests resulting in a material balance higher than 95% were considered successful.

The tests were compared on the basis of the pitch conversion, the distillate yield and the coke formation.

Six commercially available catalysts and two in-house-prepared catalysts were tested. The criteria for the catalysts selection were: a) decomposition of methanol into hydrogen and carbon monoxide and

Sommaire

La companie SANDWELL TECHNOLOGIES (Santech) a recu de la part de CANMET un contract pour éxecuter des essais préliminaires utilisant son réacteur au chargement a haute température pour le traitement du brai a l'aide du methanol. Ce procéssus est le résultat d'une idée concue a CANMET et implique la production des fraction distillables a partir du résidue de vide par hydrocraquage en presence du methanol qui agit comme donneur de hydrogéne.

Le program expérimental exécute par Santech couvra la sélection des cataliseurs et des conditions de réaction adequates, aussi que l'investigation de l'effect de ces paramétres sur la conversion de la brai.

Ce raport decrit l'équipement utilisé les procédures expérimentaux et d'analyse, les résultats economiques préliminaires et les conclusions tirées apres la fin des travaux de cette premiere phase de rechérche.

Santech a exécute 24 expériences en employant une brai fournite par CANMET et du methanol industriel. De ces 24 expériences seulement ces qui ont donné des bilans des matériaux de 95% ou plus furent considéres réussis.

Les essais furent comparés en terme des leur convérsion de la brai, leur rendement des produits distillés et le degrée de formation de coke.

Six catalyseurs commérciales et deux catalyseurs preparés dans nos laboratoires furent essaiés. Les critéres employees pour la seléction des catalyseurs furent: a) l'effect de décomposition du methanol en hydrogéne et monoxide de charbon et

b) their hydrogen transfer activity. The Molybdenum containing catalysts displayed a superior overall performance in terms of pitch conversion and distillate yield. The best results were obtained with the CoMo/CabOSil catalyst prepared by Santech.

The highest pitch conversion obtained was 68.4% and the best distillate yield was 64.8%. At least 22-27% of the pitch feed was converted into lighter distillate and 30-37% into vacuum distillate. Composite samples of the distillate product showed a hydrogen content of corresponding to a H/C atomic ratio of 1.7 compared to 1.3 in the feed.

The reaction parameters for best results were obtained were: 380°C, 120 minutes contact time and a methanol pitch ratio of 1.5 using CoMo/CabOSil catalyst.

These results are an indication of the feasibility of the methanol treatment concept, it must be noted though that due to the batch testing mode some of the results are not representative of a commercial process. Such is the case of the methanol/consumption which in a continuous reactor where the retention time of the methanol can be controlled and limited to 15 minutes, will not exceed 50% of the feed.

Other results considered meaningfuy in the evaluation of the work are:
- the Zn, Cr catalysts proved effective for the decomposition of the methanol but did not catalyse the hydrogen transfer and as a result the conversion and the distillate yield were inferior to those obtained with Co,Mo catalysts.

- the Fe containing catalysts were not effective at the conditions of this process and as a result large amounts of coke were produced.

b) l'activitée de transfére d' hydrogéne Les catalyseurs contenant du molybdéne ont donné des résultats supérieurs en ce qui concérne la conversion de la brai et le rendement des distillables. Les meilleurs résultats furent obténues avec le catalyseur cobalt, molybdene sur CabOSil preparé par Santech.

La meilleure convérsion obténue fut de 68.4% et le meilleure rendement des distilles fut 64.8%. Au moins 22-27% de la brai initiale fut converti en fractions légéres et de30 a37% en distilles de vide. Des échantillons combinés des fraction de distillation furent analysés et les résultats montrerent un contenu en hydrogen de 11.5% ce qui corésponde a un raport H/C atomique de 1.7 au temps que pour la brai d'alimentation le même fut seulement 1.3.

Les conditions de réation auxquelles les meilleures résultats furent obtenues sont: 380 deg. C température, 120 minutes temps de contact, utilisant le catalyseur CoMo/CabOSil.

Ces résultats constitues une bonne preuve que ce nouveau concépt est faisable. Il faut qu'a même remarquer que a cause des constraintes imposées par le mode de essai en charge (non continue) il y a des résultats qui ne sont pas représentatives d'un processus commerciale. C'est le cas de la rate de consomation du methanol la quelle dans une appliquation commerciale avec le réacteur en continue ou le temps de contact du methanol peut etre limite a 15 minutes, ne surpassera 50% de l'alimentation.

Autres, resultats importantes obtenues sont:
- le cataliseur ZnCr fut active pour la décomposition du methanol en hydrogéne e monoxide de charbon mais il n'a pas catalysé le transfére de l'hydrogéne et comme resultat la conversion et le rendement des distillés furent inférieures a ceux obténues avec le catalyseur de cobalt-molybdéne.
-les catalyseurs contenant du fer furent inactive aux conditions de ce procéssus et comme résultat des larges quantitées de coke se sont formées.

- the addition of water to the reaction did not result in mitigation of the coke formation, probably due to catalyst deactivation.
- the pitch conversion increased with the reaction temperature only up to 380°C after which it is assummed that the regression reactions start taking place in parallel with hydrocracking ones resulting in coke formation.

One the basis of the best results obtained, Santech looked into the economics of a plant using this concept for upgrading pitch in Alberta using methanol produced from natural gas. The economic model for the calculation of the internal rate of return of investment had been developed in-house by Santech for its own use. This report includes the results of these calculations as well as the results of a preliminary sensitivity analysis. The main findings of the economic calculations are:
- the process can be economically implemented at conditions where the hydrogen production is not economical and low cost methanol is available in the proximity of the heavy residue source.
- the IRR calculated for the best results obtained in the study is 19.79%.

The sensitivity analysis of the economic model used identified the critical variables as being the rate of methanol consumption, the price of the pitch feed and the distillate yield.

- l'addition de l'eau a la réaction n'a pas eut le résultat attendu de diminuer la formation du coke, ce qui est probablement due a la déactivation des catalyseurs en présence de l'eau.
- la conversion de la braj a augmenté avec la température jusqua 380°C mais apres ca elle diminua probablement due aux réactions de régression conduisant a la formation des coke en paralel avec la réaction de hydrocraquage.

A partir des meilleurs résultats obténues Santech a fait des études économiques préliminaires pour une usine a partir de ce processus de traitement de la brai, situee en Alberta, alimentant du methanol produit a partir du gas naturel. Le model économique pour la calculation de la rate de retour de l'invéstissement fut développe par Santech por ur son propre travail et ne fait partie du mandat de ce projét. Ce raport inclue les résultats des ces calcules aussi que les résultats de l'analyse préliminaire des facteurs critiques de point de vue économique (sensitivity analysis).
Les résultats signifficatives sont les suivantes: - le processus peut etre viable de point de vue économique dans des conditions où il n y a pas une manufacture d'hydrogéne ou si il y a du methanol a bas prix situé en proximitée de réserves de huiles lourdes. Dans ce cas la rate de retour de l'invéstissement sera de 19.79%.

Les facteurs qui sont critiques pour l'économicitée d'une usine comme ca sont la rate de consume du methanol, le prix de brai et le rendement en distillables.

INTRODUCTION

The importance of the heavy crudes and the tar sand oils as a source of hydrocarbon liquids has increasingly been recognized worldwide during the last few years.

Canada has one of the largest known reserves of bitumen recoverable from the tar sand deposits. The Athabasca deposit in Alberta is among the largest in the world.

The upgrading of these materials has been extensively investigated in recent years and various processes have been developed, each providing different degrees of conversion and quality improvement.

Pitch, with a boiling point above 525°C, is a heavy residue from refining/upgrading processes. Because of its high contents of sulfur and metals, pitch cannot meet the Canadian combustion specifications, and is not suitable as a starting material for making electrode coke. One common usage is to mix the pitch with a flux to make heavy industrial fuel oil (bunker oil). Today, there is a tendency to convert combustion units to burn coal instead of bunker oil. As a result, pitch will be in less demand on the market.

It is expected that a considerable amount of pitch will be produced by processes used in upgrading the bitumen from oil sands. As demand for more liquid product intensifies, the hydrocracking processes will be utilized to upgrade the bitumen in commercial plants. These hydrocracking processes will produce 5-10% pitch as a by-product. The storing or disposal of the pitch has been identified as one of the problems in future operations.

The present commercial uses of the pitch are for production of:
- aphalt (road, roofing, pipe insulation)
- coke
- bunker oil

The technologies commercially used for upgrading the pitch are mainly based on coke rejection such as delayed coking and flexicoking, Cherry P or Eureka.

Under study are other routes for pitch conversion into usable products and these are direct gasification for synthesis gas production and a combination of pyrolysis and gasification.

As part of the effort to establish new technologies for conversion of the pitch into marketable liquids, CANMET initiated in 1984 a research program for the use of methanol for upgrading of the 525° + C pitch into distillable products.

Sandwell Technologies was awarded a research contract for preliminary work using autoclave reactors in batch mode. The objectives of this progam were to investigate the applicability of the pitch upgrading with methanol concept, conduct catalyst screening and study the effect of reaction parameters upon the pitch conversion. Such parameters investigated were:

- Reaction Temperature
- Methanol Pitch Ratio
- Type of Catalyst
- Introduction of Steam in the reactor
- Reaction Time

The results obtained were very exciting. It was found that using cobalt-molybdenum catalysts of large pore structure, a conversion of 68% of the pitch feed was consistently obtained at temperatures as low as 380°C, without formation of coke and very low (less than 4%) production of gas. At the conclusion of this program, it is believed that both the pitch conversion and distillate yields can be increased by operating in continuous mode and that by judicious design of the reactor the methanol consumption and the process pressure can be lowered.

The pitch used in this study was the fraction of the Athabasca bitumen with a boiling point above 524°C.

An extensive literature search was carried out as the initial task in order to select the most suitable catalysts and process conditions for the processing of pitch with methanol.

The testing, carried out in a 2-liter autoclave reactor in batch mode, was focused on the screening of the catalysts and the effects of reaction temperature, reaction time and methanol/pitch ratio on the pitch conversion.

The effectiveness of each catalyst was evaluated by the pitch conversion, the distillate yield, the product distribution, the consumption of methanol and the coke formation.

2. REVIEW OF LITERATURE

In preparation of the experimental work under this contract Santech undertook an extensive review of the literature. The objective of this review was to locate previous published work using methanol as hydrogen donor and also to review the present state of the art in pitch upgrading, identify the catalysts and process conditions.

Particular emphasis was placed on the selection of the catalysts due to the multiple function which the catalyst had to exhibit in order to form hydrogen by decomposing methanol and at the same to crack the high-molecular asphaltene species into smaller fragments and to hydrogenate the unstable fragments to prevent polymerization reactions.

More than 300 references and 35 patents were identified by on-line computer search, using the CANOLE system to access the Alberta Oil Sands Information (AOSI) and Chemical Abstracts data bases.

The literature directly related to the requirements of this work was critically reviewed and the information obtained, along with Santech experience formed the basis for the selection of the catalysts, techniques for catalyst preparation, range of operating conditions, operating procedures, and methods for the recovery, analysis and characterization of the product.

A limited number of articles related to the use of lower alcohols as hydrogen donors were found and they all involved the liquefaction of coal. This work was reviewed and the findings will be extended to the pitch upgrading using methanol.

The literature cited is listed below under the following subjects:

- Use of Alcohols as H-Donors in Coal Liquefaction
- Methanol Properties and Reactions
- Chemical Characterization of Bitumen
- Bitumen Hydroprocessing - Heavy Crudes Upgrading
- Hydrocracking Catalysts - Catalyst Activity and Aging

Each reference is presented by its title, authors, journal and abstract.

USE OF ALCOHOLS AS H-DONORS IN COAL LIQUEFACTION

1. COAL LIQUEFACTION BY THE HYDROGEN PRODUCED FROM METHANOL
   MODEL COMPOUND STUDIES.
   Fanor Mondragon, Ryuji Kamoshita, Takashi Katoh, Hironori Itoh and Koji Ouchi
   Fuel, Vol. 63, May 1984.

   Coal can be converted into a material soluble in solvents using methanol as an in-situ hydrogen source and also as an alkylating agent. This paper presents the results of the reaction of selected model compounds with methanol using two different hydrogenation catalysts: stabilized nickel at 365°C, and stabilized cobalt at 405°C and 445°C. Stabilized nickel is a much better catalyst than stabilized cobalt. The alkylation reaction is strongly dependent on the presence of specific functional groups (-OH,-NH,etc.). Also the alkylation reaction appears to be independent of the hydrogenation catalyst used and it seems to depend more on the temperature. The alkylated products from the reactions at 405°C showed an order as follows: carbazole>phenol>phenanthrene>dibenzofuran>diphenylether> dibenzothiophene>diphenylmethane. A free radical mechanism is proposed for the alkylation reaction.

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2. COAL LIQUEFACTION BY THE HYDROGEN PRODUCED FROM METHANOL
   Fanor Mondragon, Masataka Makabe, Hironori Itoh and Koji Ouchi.
   Fuel, Vol. 61, April 1982.

   Methanol was used as an in-situ source, following its decomposition over $ZnO-Cr_2O_3$, for the hydrogenation of coal. The reaction was carried out in a high pressure autoclave at 400-440°C, in the presence of different hydrogenation catalysts. Stabilized nickel, stabilized Co and Ni-Cr-Cu catalysts gave excellent results. The maximum conversion was 100% for pyridine, 94.4% for benzene and 66.2% for straight-chain hexane.

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3. COAL LIQUEFACTION BY HYDROGEN PRODUCED FROM METHANOL
   EXAMINATION OF REACTION CONDITIONS
   Yoshihide Ozaki, Fanor Mondragon, Masataka Makabe, Hironori Itoh
   Fuel, June 1985, Vol. 64, p767-771

   Coals were liquefied in a 50 ml autoclave using hydrogen produced from methanol with decomposition and hydrogenation catalysts under various conditions. The conversion increased with increasing reaction temperature and time. This reation is more suitable for the liquefaction of lower-rank coals. The hydrogen pressure had little effect on the conversion in the range of the ratio of methanol to coal of 2 g/g. The use of a solvent is very effective in increasing the liquefaction, especially at short times.

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4. SOLUBILITY INCREASE OF COALS BY TREATMENT WITH ETHANOL
Masataka Makabe and Koji Ouchi.
Fuel Processing Technology 5(1981) 129-139

The coals were treated with ethanol at a temperature higher than 380°C and the effect of the reaction conditions, such as initial nitrogen pressure, temperature and the time were examined. The higher reaction temperature gave higher solubility of the product in solvents, but the reaction at a still higher temperature reduced the solubility of the product. The temperature giving the maximum solubility increased from the lower rank of coals to the higher rank of coals and the maximum extraction yield decreased with increasing coal rank. The higher initial pressure of nitrogen gave higher solubility of the product in the solvents and this may be caused by higher density of ethanol under higher pressure. In 1 hour the reaction reached equilibrium. At 420°C the products from the lower rank coals dissolved nearly completely in pyridine, but the products using coals with greater than 83% carbon rapidly reduced the solubility in pyridine.

The reaction mechanism was estimated from structural analysis, IR spectra, measurement of molecular weight and ultimate analytical values. Considering these data, the alkylation with ethanol and the splitting of ether linkages will be the main mechanism of this reaction.

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5. ALCOHOLS AS H-DONOR MEDIA IN COAL CONVERSION
1. BASE-PROMOTED H-DONATION TO COAL BY ISOPROPYL ALCOHOL
David S. Ross and James E. Blessing.
Fuel, Vol. 58, June 1979.

Isopropyl alcohol can act as a hydrogen donor to coal, the same way as tetralin. In contrast to tetralin, however, the transfer of hydrogen by the alcohol can be promoted by the presence of either potassium isopropoxide or KOH. Acetone is formed from the alcohol in quantities that agree with the amounts of hydrogen transferred to the coal. In runs at 335°C for 90 min, coal was converted with isopropyl alcohol in the presence of either the alkoxide or KOH to a fully pryidine-soluble product with H/C ratios from 0.88 to 1.13, in contrast to coal (0.79). The organic sulphur content of the coal was reduced from 2.1% to 1%. Model-compound studies with anthracene and diphenyl ether showed that the anthracene was reduced in the system to 9,10-dihydroanthracene, but the ether was recovered unchanged. The coal products from the alcohol/base treatment are very rich in aliphatic hydrogen and have number-average molecular weights in the 450-500 range. The scheme suggested to explain the conversion at 335°C includes initial hydrogenation of anthracene-like structures in the coal, followed by thermolysis of the dihydro-intermediate.

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6. ALCOHOLS AS H-DONOR MEDIA IN COAL CONVERSON
2. BASE-PROMOTED H-DONATION TO COAL BY METHYL ALCOHOL
David S. Ross and James E. Blessing.
Fuel, Vol. 58, June 1979.

At 400°C in 20 min runs, coal was converted by methanol/KOH systems to a product which was extractable by pyridine fully, and 15-25% by methanol. The methanol-soluble fraction is significantly enriched in hydrogen relative to the starting coal, reduced in both N and organic S, and was fluid at room temperature. It was established that this liquid product was derived from the coal, and not the methanol. The liquid was distillable at 300°C/133 Pa (1 torr), and the analysis of the liquid by gas chromatography/mass spectrometry techniques shows it to consist of significant quantities of butyrolactone, polymethyl phenols, and some unidentified compounds having major C_4H_7O and $C_4H_7O_2$MS fragments. The methanol-insoluble products were hydrogen-enriched also, but to a lesser degree. The suggested conversion scheme is similar to that proposed for isopropyl alcohol, where alkoxide ion donates hydride to the coal, followed by proton abstraction by the anionic intermediate from the alcohol medium. In model-compound studies at 400°C with the system, it was found that phenyl ether was converted in 33% yield to a collection of polymethyl phenols, similar to those found in the coal distillate. Anthracene was converted in about 80% yield to 9,10-dihydroanthracene. Bi-phenyl ether, phenanthrene and bibenzyl were found to be unreactive in the system.

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7. SOLUBILITIES OF TAIHEIYO (Japan) COAL IN A SERIES OF ALCOHOLS
Fanor Mondragon, Masataka Makabe, Hironori Itoh and Koji Ouchi.
Fuel, Vol. 60, October 1981.

High conversions of coal to pyridine-soluble materials have been achieved with ethanol as reaction medium. This reaction is highly favourable for coal dissolution because the recovery of the alcohol is very easy and the product can be extracted by other solvents at atmospheric pressure at relatively low temperatures. Moreover, this reaction does not need any hydrogen gas and the product does not contain any other materials except the coal itself. Ouchi et al. using model compounds to elucidate the reaction mechanisms, found that cleavage of ether bonds, hydrogenation of aromatic nuclei and some alkylation are the reasons for this high solubilty. Also they found that the solubility of the product in pyridine, benzene and ethyl alcohol, for the ethyl alcohol treated coals, increased with increase in nitrogen pressure.

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8. DISSOLUTION OF COAL WITH NaOH-ALCOHOL: EFFECT OF ALCOHOL SPECIES
Koji Ouchi, Horoshi Ozawa, Masataka Makabe and Hironori Itoh.
Fuel, Vol 60, June 1981.

Methanol, ethanol, straight-chain propanol, isopropanol, straight-chain butanol, sec-butanol, tert-butanol, straight-chain pentanol, and iso-pentanol were used for the reaction of coal with NaOH-alcohol at 290°C for 1 h. All the products dissolved in pyridine with an extraction yield of 80 wt%. Straight-chain alcohols are less reactive than the secondary alcohols due to the differences in hydrogen donating ability.

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9. SOLUBILITY INCREASE OF COAL BY ALKYLATION WITH VARIOUS ALCOHOLS
Fanor Mondragon, Hironori Itoh and Koji Ouchi.
Fuel, Vol. 61, November 1982.

A vitrinite concentrate of Taiheiyio coal has been reacted with various alcohols using $ZnCl_2$ as a catalyst under nitrogen pressure. The reaction conditions such as the reaction time, reaction temperature, initial nitrogen pressure and the effect of other Lewis acids as catalysts have been examined using ethanol. The product from the reaction with methanol at 400°C is fully soluble in pyridine, 57% in benzene and 26% in straight-chain hexane. This result is similar to that obtained when coal is hydrogenated under 10 MPa hydrogen pressure, Higher temperature, higher initial nitrogen pressure and longer rection times give increased solubility. $ZnCl_2$ and $FeCl_3$ are the best catalysts. Of the various alcohols, branched alcohols give better results.

* * * * *

10. SOLUBILITY INCREASE OF COALS BY THE REACTION WITH ALCOHOL
- ELUCIDATION OF REACTION MECHANISM USING MODEL COMPOUNDS
Masataka Makabe and Koji Ouchi.
Fuel Processing Technology, 6(1982) 307-316.

The reaction mechanism of coal-ethanol reation was examined using model compounds: phenol, benzylphenylether, diphenylmethane and anthracene. The main reaction for these compounds was the splitting of ether bonds, ethylation of benzene nucleii, hydrogenation of aromatic nucleii and the splitting of methylene linkages. The most important reactions were the first two types. The splitting of ether linkages would reduce the molecular weight of coal and ethylation of aromatic rings would be favourable to the easy dissolution of coal in solvents.

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11. EFFECT OF PRESSURE AND TEMPERATURE ON THE REACTION OF COAL WITH ALCOHOL-ALKALI
Masataka Makabe and Koji Ouchi.
Fuel, Vol. 60, April 1981.

The ethanol-NaOH reaction of Taiheiyo coal (C,77.5;H, 6.3 wt%) was examined under a pressure of 0.1-8 MPa nitrogen or hydrogen at 300°C for 1 h. Almost all of the products were extracted with pyridine for the entire pressure range and the extraction yield with ethanol increased with pressure, even under nitrogen. The yield of the products extracted with ethanol was higher when the coal reacted under hydrogen than when reacted under nitrogen. The explanation for these results is that, under pressure, the hydrogen produced from the reaction of alcohol and NaOH is enclosed for a longer period in the solvent, thus accelerating the hydrogenation reaction of the coal, also under hydrogen pressure, the reaction is particularly accelerated because the hydrogenation takes place with the hydrogen gas. At 300°C, the ethanol-extraction yield is much higher than the benzene extraction yield, but the latter increases rapidly and approaches that of the ethanol-extraction yield as the temperature rises to 400°C. This is because the polar groups, e.g., as hydroxyl groups which are rich in the low-temperature products, decrease with the temperature increase.

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12. REDUCTION OF COAL WITH HEXAMETHYLPHOSPHORAMIDE-Na-t-BuOH
Koji Ouchi, Soyoko Kotani, Masataka Makabe and Hironori Itoh.
Fuel Processing Technology, 5(1981) 119-128

Two coals (87.5%C and 91.5%C) were reduced at room temperature using hexamethylphosphoramide-Na-t-Butanol. Nearly 80% of the coals could dissolve after reducing the insoluble part in pyridine once or three times. The reaction was repeated two or three times for these pyridine extracts. It was observed from infra-red or nuclear magnetic resonance spectroscopy that the reduction proceeded with the repeat of the reaction. From the structural analysis the total ring number (aromatic and naphthenic)per structural unit of 87.5%C coal was estimated to be 4-6 and that of 91.5%C coal to be 7-14.

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METHANOL PROPERTIES AND REACTIONS

13. HYDROGEN PRODUCTION BY THE CATALYTIC STEAM REFORMING OF METHANOL
Part 2. KINETICS OF METHANOL DECOMPOSITION USING GIRDLER G66B CATALYST
J.C. Amphlett, M.J. Evans, R.F. Mann and R.D. Wier.
The Canadian Journal of Chemical Engineering, Vol. 63, August 1985.

The rate of catalytic decomposition of methanol in the presence of steam has been studied using a commercial Girdler G66B CuO-ZnO low temperature shift catalyst from 150 to 250°C at atmospheric pressure. The molé ratio of steam to methanol was varied from 0 to 1.5, and the feed rates covered the range from 300 to 1400 kgs/mol. The data were sucessfully correlated using a simple reaction network involving CH_3OH, H_2O, CO and H_2. A conventional reversible reaction rate equation was used which included a resistance term for site blockage by a CO surface complex. The methanol decomposition rate constants showed satisfactory Arrhenius behaviour with an activation energy of about 96 kJ/mol.

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14. KINETIC MODEL FOR METHANOL CONVERSION TO OLEFINS
Raul Mihail, Sorin Straja, Gheorghe Maria, Gavril Musca, and Grigore Pop
Ind. Eng. Chem. Process Des. Dev., Vol. 22, No. 3, 1985.

This paper deals with a phenomenogical model for methanol conversion to olefins. a system of linear independent reactions is built from the global reaction of methanol transformation. The mechanism of reaction, a development based on carbenoid intermediates of the above set of chemical reactions, has 27 reactions and 18 molecular species. The kinetic parameters identified using nonlinear optimization techniques, and the model predictions, agree satisfactorily with experimental data and data available in the literature.

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15. DEHYDROGENATION OF METHANOL TO MEYTHYL FORMATE OVER COPPER CATALYSTS
Stephen. P. Tonner, David L. Trimm, Mark S. Walnwright, and Noel W. Cant.
Ind. Eng. Chem. Prod. Dev., 1984, 23, 384-388.

The suitability of a number of copper catalysts for the hydrogenation to methyl formate has been assessed via the use of specific rate constants, based on metal surface areas, for the dehydrogenation reaction, and the major side reaction, decarbonylation. Copper chromite catalysts, which combine high bulk densities with high metal areas, were particularly effective despite the existence of a negative contribution of the support to specific activity which was low when compared with copper on silica catalysts. Raney copper catalysts gave very high initial activity, but rapid deactivation took place. This was attributed to polymerization of a formaldehyde intermediate in the reaction scheme.

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16. DECOMPOSITION OF ALCOHOLS OVER ZIRCONIUM AND TITANIUM PHOSPHATES
Soofin Cheng, Guang Zhi Peng, and Abraham Clearfield.
Ind. Eng. Chem. Process Des. Dev., 1983, 22, 538-544

The catalytic properties of the layered compounds - zirconium phosphate, titanium phosphate, mixed zirconium titanium phosphate, and their originally pillared derivatives - toward methanol conversion have been examined. Dimethyl ether was found to be the precursor for hydrocarbon formation. However, strong acidities of the phosphate compounds seem to enhance methane formation. The phenyl-group bridged derivatives were found to have remarkably higher catalytic activities and selectivities for the conversion of methanol to low molecular weight hydrocarbons. These pillared compounds were considered to provide pore structure for shape-selective products. Moreover, the phenyl pillars were suggested to be capable of stabilizing reaction intermediates.

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17. THE HIGHER ALCOHOL SYNTHESIS OVER PROMOTED Cu/ZnO CATALYSTS
Kevin J. Smith and Robert B. Anderson.
The Canadian Journal of Chemical Engineering, Volume 61, Feb. 1983.

Alkali oxides added to methanol catalysts increase the formation of ethanol, n-propanol and isobutyl alcohol. This result has been known for many years, yet few quantitive studies have been reported in the literature. Data obtained on a commercial copper-zinc oxide catalyst promoted with K_2CO_3 are presented and compared with published work. The optimum promoter concentration was about 0.5% by weight. The H_2 to CO feed ratio was important in determining the higher alcohol selectivity. The rate of production of isobutyl alcohol varied as $pH_2\ p_{CO}$ while for methanol, ethanol and n-propanol both exponents were positive and less than 1.6. Decreasing the hydrogen to carbon monoxide ratio from 2 to 0.5 more than doubled the isobutyl alcohol selectivity. Chain growth schemes predicting the higher alcohol selectivity are presented and estimates of the parameters are given.

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18. METHYLATION OF PROPENE IN THE CONVERSION OF DIMETHYL ETHER (OR METHANOL) TO HYDROCARBONS
Rafael L. Espinoza
Ind. Eng. Chem. Prod. Dev., 1984, 23, 449-452

Propene is the most reactive primary olefinic product formed when methanol or dimethyl ether (DME) reacts over an acid silica-alumina catalyst. Further conversion of propene occurs by methylation and oligomerization. Experiments with mixed DME-propene feeds at 1.7 bar, 150 to 380°C, and mass hourly space velocities (MHSV) of 3.9 to 4.1 demonstrate that for low to medium feed concentrations of DME (20 to 80%) oligomerization is the dominant growth mechanism, in contrast with published reaction schemes. The oligomerization/methylation ratio can be related directly to the DME concentration.

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CHEMICAL CHARACTERIZATION OF BITUMEN

19. COMPARISON OF THE CHEMICAL STRUCTURE OF COAL HYDROGENATION PRODUCTS, ATHABASCA TAR SAND BITUMEN AND GREEN RIVER SHALE OIL
R. Yoshida, Y. Nakata, Y. Hasegawa, M. Hino, Y. Ikawa, M. Makabe and D.M. Bodily
Fuel Process Technology, 7(1983) 161-171

Coal hydrogenation products, Athabasca tar sand bitumen, and Green River shale oil produced by retorting were analyzed by the Brown-Ladner method and the Takya et al. method on the basis of elemental analysis and proton H-NMR data, ^{13}C-NMR spectroscopy and by FT-IR spectroscopy. Structual characteristics were compared.

The results show that the chemical structure of oils from Green River shale oil and Athabasca tar sand bitumen, and the oils produced in the initial stage of hydrogenation of Taiheiyo coal and Clear Creek, Utah coal is characterized by monomers consisting of units of one aromatic ring substituted highly with C_{5-6} aliphatic chains and heteroatom-containing functional groups. The chemical structure of asphaltenes from Green River shale oil and Athabasca tar sand bitumen is characterized by oligomers consisting of units of 1-2 aromatic rings substituted highly with C_{5-6} aliphatic chains and heteroatom-containing functional groups. The chemical structure of asphaltenes from coal hydrogenation is characterized by dimers and/or trimers of unit structurs of 2 to 5 condensed aromatic rings, substituted moderately with C_{2-5} aliphatic chains and heteroatom-containing functional groups.

The close agreement between fa(^{1}H-NMR) and fa(^{13}C-NMR) for Green River shale oil derivatives and Athabasca tar sand derivatives indicates that the assumption of 2 for the atomic H/C ratio of aliphatic structures is reasonable. For coal hydrogenation products, a value of 1.6-1.7 for the H/C ratio of aliphatic structures would be more reasonable.

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20. SOME RECENT ADVANCES IN THE CHEMISTRY OF OIL SAND BITUMEN
O.P. Stausz
First International Conf. on the Future of Heavy Crude and Tar Sands, Edmonton, 4-12 June 1979. P 187-194 (8)

A more in-depth understanding of the chemistry of various types of bitumens and their reactions to the geoenvironment are necessary in a successful commercial recovery of these resources. More refined analytical methods are devised to reach these goals.

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21. ASSOCIATION-DISSOCIATION PROBLEMS IN CHARACTERIZING ASPHALTENES IN COAL LIQUIDS
R.G. Ruberto, D.C. Cronauer and L.G. Galya
Fuel Processing Technology, 5(1981) 103-118

The determination of asphaltenes in coal liquefaction products is strongly related to the chosen solvents, extraction time, sequence of extractive solvents, and co-solvent effects of the coal liquids. Recognizing that asphaltenes as operationally defined, the above observations raise the question of whether there are "asphaltenes" in the unseparated coal liquids or whether they are artifacts of the separation procedure, resulting from the association of unstable, reactive molecules that combine upon their concentration and isolation from the original slurry. Using preparative and analytical Gel Permeation Chromatography and solvent extraction procedures, qualitive molecular size profiles of coal liquid products have been obtained. It has been concluded that: (1) the pre-asphaltenes, asphaltenes and oils exist in the coal liquids, and are not artifacts of the separation procedures; (2) their molecular sizes follow the order pre-asphaltenes> asphaltenes>oils; (3) association-dissociation of the coal liquids is indicated and (4) coal liquid fractions obtained by different methods should not be considered equivalent.

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22. INFLUENCE OF THERMAL PROCESSING ON THE PROPERTIES OF COLD LAKE ASPHALTENES: THE EFFECT OF DISTILLATION
Kenneth A. Gould and Martin L. Gorbaty
American Chemical Society, Thermal Processing Oil Shale, Tar Sands, and Related Materials, 1981.

A better understanding of the composition and properties of heavy feeds such as Cold Lake and Arabian Heavy oils is central to the the development of improved upgrading technology. An important question which must be answered is to what extent these materials are thermally altered during refinery distillation. These heavy oils already contain large percentages of refractory materials such as asphaltenes, and it would be highly undesirable to increase the amount or degrade the quality of these components. The effect of heat treatment during distillation on the quantity and physical and chemical properties of asphaltenes were investigated. Cold Lake crude was chosen for this study since it is known to be a thermally sensitive material. Any changes caused by thermal treatment should, therefore, be more obvious than with a more stable feed. The results of a variety of measurements made on the asphaltenes isolated from Cold Lake crude oil and from its vacuum distillation residue were reported. It should be born in mind that Cold Lake crude is subjected to the high temperatures of pressurized steam used in the production process and may conceivably have already undergone some thermal alteration. The present study, however, was designed primarily to learn if any further changes might occur during refining.

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23. THE INFLUENCE OF CRUDE OIL COMPOSITION ON THE NATURE OF THE UPGRADING PROCESS: ATHABASCA BITUMEN
Speight, J.G., Moschopedis, S.E.
First International Conf. on the Future of Heavy Crude and Tar Sands, Edmonton, Alberta, 4-12 June 1979, p 603-611

Bitumen separation and upgrading are described. Special reference is made to the behaviour of asphaltene fraction during the hot water separation and the thermal methods of upgrading. Projections can also be made of asphaltene behaviour during in-situ recovery techniques. (Author abstract).

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BITUMEN HYDROPROCESSING - HEAVY CRUDES UPGRADING

24. HYDROCRACKING OF BLENDS OF CONVENTIONAL AND TAR SANDS FEEDSTOCKS
Ledas, A.E.
33rd Canadian Chemical Engineering Conf. Can Soc. Chem. Eng., Toronto 2-5 Oct. 1983. p 810-805 (6)

A research program has evaluated the processibility of blends of conventional hydrocracker feed and tar sands gas oil by two-stage hydrocracking. Commercial processing conditions were applied over a commercial denitrogenation catalyst and an amorphous cracking catalyst.

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25. HYDROGEN DONOR SOLVENT CRACKING OF ATHABASCA BITUMEN
Belinko, K., Cheung, L.Y., Hogan, T.E., Pruden, B.B.
2nd International Conf. on Heavy Crude and Tar Sands Proc, United Nations Institute for Training and Research, Caracas, 7-17 Feb. 1982, p 1268-1273 (7)

The hydrogen donor solvent cracking (HDSC) concept has been extensively investigated for coal liquefaction. In contrast, relatively little research has been carried out on HDSC of tar sands bitumen and heavy oils. The hydrogen donor solvent could be used to extend the range of operability (i.e., suppress coke formation) during hydrocracking of Athabasca bitumen. In a series of continuously stirred tank-reactor runs at moderate hydrogen pressure, the operability was exteneded from 50 percent pitch conversion in the absence of H-donor solvent to close to 80 percent pitch conversion with a feed to tetralin ratio of 1:1. These findings suggest that feedstocks that are difficult to hydrocrack, because of high coking propensity, can be processed relatively easily using donor solvent. Results are discussed with reference to existing hydrocracking technologies. (author abstract).

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26. COMPARISON OF COKING AND HYDROCRACKING FOR UPGRADING ATHABASCA BITUMEN
Ring, T.A., Benz, A.D., Starr, J.J.
2nd International Conf. on Heavy Crude and Tar Sands Proc, United Nations Institute for Training and Research, Caracas, 7-17 Feb 1982, p 1218-1226 (10)

Four upgrading routes (delayed coking, flexicoking, fluid coking, hydrocracking) are evaluated and compared for their capital/operating costs, as well as products yield and quality. Hydrocracking requires higher operating cost than the other processes, but it also offers higher yield.

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27. UPGRADING BY HYDROCRACKING: SELECTED AREAS OF R & D INTEREST AT CANMET
Kriz, J.F., Ternan, M., Denis, J.M.
2nd International Conf. on Heavy Crude and Tar Sands Proc., United Nations Institute for Training and Research, Caracas 7-17 Feb 1982, p 1221-1217 (8)

Recent findings on the CANMET conversion reactions during thermal hydrocracking and catalytic hydrocracking of heavy feedstocks are reported in this paper. The logistics of co-processing bitumen/heavy oil with coal are also investigated.

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28. THE CANMET RESIDUUM HYDROCRACKING PROCESS: AN UPDATE
Chambers, L.W., Waugh, R.J., Silva, A.E., Denis J.M.
2nd International Conf. on Heavy Crude and Tar Sands Proc, United Nations Institute for Training and Research, Caracas 7-17 Feb 1982, p 1206-1210 (6)

As a first step towards commercialization, CANMET is integrating a 5,000 BPSD hydrocracking unit to an existing refinery in Montreal to treat vacuum residues from various feedstocks. Other areas of development include process optimization, feed characterization, alternate utilizations of pitch, and the design of an upgrader for Cold Lake bitumen.

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29. APPLICATION OF KOMBI HYDROGENATION AND DONOR-SOLVENT HYDROVISBREAKING FOR THE UPGRADING OF ORINOCO HEAVY CRUDES.
Graeser, U., Herbertz, H., Galiasso, R., Martin, J.
2nd International Conf. on Heavy Crude and Tar Sands Proc, United Nations Institute for Training and Research, Caracas, 7-17 Feb 1982, p 1155-1165 (12)

The development of German hydrogenation technology which started in 1913 is reviewed. A description of two possible hydrogenation routes for the upgrading of Orinoco heavy oil is given. The Veba-Kombi-hydrogenation is a direct combination of liquid and gas phase reactor systems which results in a high thermal efficiency for the overall process. The donor-solvent hydrovisbreaking process (DSV) developed by Lurgi in association with Intevep. S.A. (R & D center of Petroleos de Venezuela S.A.) uses a hydrogen donor-oil in order to reduce the amount of necessary hydrogen.

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30. COST CONSIDERATIONS IN HEAVY CRUDE PROCESSING
Lutz, I.H.
2nd International Conf. on Heavy Crude and Tar Sands Proc, United Nations Institute for Training and Research, Caracas, 7-17 Feb 1982, p 1111-1119 (10)

High asphaltene conversion, low coke yield and cost are the main criteria in this review and discussion of the merits of different upgrading routes for heavy crudes and residues. Further utilization and conversion of the produced coke and resids from the above processes are also investigated.

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31. 1155385 PATENT - CANADA, PROCESS FOR HYDRODEMETALLIZATION OF HYDROCARBON STREAMS
Bertolacini, R.J.
Standared Oil Company, Dec. 27, 1983 (23)

This patent proposes a catalytic hydrodemetallization process using a catalyst comprising one or more transition metals (cobalt, molybdenum, nickel, tungsten) on a porous glass support.

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32. ASPHALTENE CRACKING IN CATALYTIC HYDROTREATING OF HEAVY OILS. 3.1. CHARACTERIZATION OF PRODUCTS FROM CATALYTIC HYDROPROCESSING OF KHAFJI VACUUM RESIDUE
Shiroto, Y., Nakata, S., Fukui, Y., Takeuchi, C.
Ind. Eng. Chem. process Des. Dev. V 22, N 2, 1983, p 248-257 (10)

The properties and chemical structures of asphaltenes derived from the Middle East and Venezuelan heavy oils and from Athabasca bitumen were studied before and after the asphaltenic bottom cracking (ABC) process. Examples of a high degree of heavy oil refining by ABC and solvent deasphalting (SDA) are described. The combination of ABC and SDA was found efficient for a complete conversion of asphaltenic bottoms. The paper covers detailed analyses of deasphalted oil (DAO) and SDA asphalt as well as analyses of each hydrocarbon type which was separated from DAO by centrifugal liquid chromatography.

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33. ASPHALTENE CRACKING IN CATALYTIC HYDROTREATING OF HEAVY OILS. 2.1. STUDY OF CHANGES IN ASPHALTENE STRUCTURE DURING CATALYTIC HYDROPROCESSING
Asaoka, S., Nakata, S., Shiroto, Y., Takeuchi, C.
Ind. Eng. Chem. Process Des. Dev. V 22, N 2, 1983, p 242-248 (7)

Characteristics in catalytic conversion of asphaltenes in petroleum heavy residues were studied in the hydrotreating process. A Boscan crude, an Athabasca bitumen, and a Khafji vacuum residue were tested as typical feestocks. Various analyses were made to obtain the properties of asphaltenes before and after the reaction, e.g., changes of heteroatoms such as sulfur and metals, and decreases of molecular weight, the characteristic changes of asphaltene molecules were also investigated by electron spin resonance (ESR) and X-ray analyses. The association and co-ordination of vanadyl in asphaltenes were studied by the temperature dependence on the ESR spectra, and the sizes of the stacked crystallites and the aggregated asphaltene micelles were measured with X-ray diffraction and small-angle scattering. In the asphaltene cracking mechanism, it was clarified that the main reactions were the destruction of asphaltene micelles caused by vanadium removal and the depolymerization of asphaltene molecules by removal of heteroatoms such as sulfur. (author abstract).

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34. ASPHALTENE CRACKING IN CATALYTIC HYDROTREATING OF HEAVY OILS. 1.1. PROCESSING OF HEAVY OILS BY CATALYTIC HYDROPROCESSING AND SOLVENT DEASPHALTING
Takeuchi, D., Fukui, Y., Nakamura, M., Shiroto, Y.
Ind. Eng. Chem. Process Des. Dev. V 22, N 2, 1983, p 236-242 (7)

A new catalytic hydrotreating process, the asphaltenic bottom cracking (ABC) process, for heavy residual oils has been investigated and the relation between catalysts and chemical structure. A proprietary catalyst has been developed which is capable of hydrocracking asphaltenes into heptane-soluble materials and decreasing the vanadium content of heavy crudes and residues at a lower hydrogen consumption than a commercial hydrodesulfurization (HDS) catalyst and without change in activity in a six-month test. Various heavy feedstocks were tested in a catalytic reactor (ABC section) and a solvent deasphalting unit (SDA). Precipitated asphaltenes were recycled. Reactivities of various residues and the proposed mechanism are discussed. This ABC process will be most useful as a step preceeding an existing hydrocracking process in the upgrading of residues with high asphaltenes and metal contents. In addition, the application of this technology is described. (author abstract).

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35. EFFECT OF HYDROCRACKING ON THE DISTRIBUTION OF NITROGENOUS COMPONENTS IN ATHABASCA BITUMEN
Sawatzky, H., Beshai, J.E., Smiley, G.T., George A.E.
Energy Mines and Resources Canada, CANMET Report 79-20, Mar. 1979, (16)

The effect of hydrocracking on the distribution of nitrogenous components in Athabasca bitumen was investigated by studying products obtained at different severities. The components were separated by chromatography on anion and cation exchange resins using a modified method developed in connection with API project. 60. The various fractions of nitrogenous and associated polar compounds were examined using infrared spectrometry and titration of the bases. Infrared data showed that carbazoles, indoles and related compounds, particularly in the asphaltenes increased substantially with hydrocracking severity. Basicity of the hydrocracked products which, too, increases with severity, is also discussed. (author abstract).

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36. 4125455 PATENT - U.S. HYDROTREATING HEAVY RESIDUAL OILS
Herbstman, S.
Texaco Inc., Nov. 14, 1978, (4)

Low concentrations of group VIB metal salts of fatty acids will catalyze the hydroconversion of sulfur-containing heavy petroleum oils producing a lighter oil fraction having a lower sulfur concentration than the heavy oil and tar fraction containing a higher sulfur concentration than the heavy oil. Catalyst concentrations of 300 to 1,000 PPM, calculated as the elemental metal, are used. Molybdenum octoate is a preferred catalyst. (author abstract)

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37. HOW TO UP GRADE HEAVY FEEDS:
More heavy crudes and less demand for residual oils make upgrading a vital subject for examination.
B. Schuetze, H. Hofmann
Hydrocarbon Processing, February 1984.

An overview of the published processes for the upgrading of heavy crudes and residual oils and the fundamental connections between their developments. The upgrading processes are grouped into catalytic hydroprocesses, Non-catalytic hydroprocesses, catalytic cracking and thermal processes. Conversion, process conditions and product yields were summarized.

38. SOME EFFECTS OF CARBON MONOXIDE IN HYDROPROCESSING OF HEAVY FEEDSTOCKS

J.F. KRIZ

Fuel Processing Technology, 8 (1983) 95-108
Elsevier Science Publishers B.V., Amsterdam - Printed in the Netherlands.

Experiments undertaken to determine the effect of the presence of carbon monoxide (CO) in the hydrogen stream on the hydrocracking of Athabasca bitumen in a high-pressure continuous-flow system showed that CO content up to 50 mol % in the hydrogen feed would not affect thermal hydrocracking detrimentally. The use of a catalyst with stabilizing capability emphasized the apparent non-interference of CO with thermal cracking. On the other hand, significant performance inhibition of molybdenum - containing multi-functional catalysts indicated surface poisoning by CO adsorption which was partially alleviated in the presence of steam. On the addition of water to the feedstock, the latter catalysts caused substantial water-gas shift reaction to take place, accompanied by less extensive methanation. These reactions were less apparent with the other type of catalysts. Depending upon feedstock characteristics it may be possible to incorporate catalytic components allowing the presence of CO in the feed. In the overall evaluation, other important effects of CO presence would have to be examined in connection with the coking propensity of the feedstock and the reactor temperature control.

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39. CATALYTIC CONVERSION OF HIGH METALS FEEDSTOCK
US PATENT 41002557, Jan 11, 1977.

Owen et al.

The conversion of high metals containing feed stock is accomplished in the presence of a low molecular weight carbon-hydrogen fragment contributing material and an acid function crystalline zeolite catalyst to produce gasoline of high quality and yields superior to that obtained heretofore.

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40. THE INFLUENCE OF CRUDE OIL COMPOSITION ON THE NATURE OF THE UPGRADING PROCESS: ATHABASCA BITUMEN

J.G. Speight and S.E. Moschopedis

The future of Heavy Oils and Tar Sands, chapter 67, 1st International conference Alberta, Canada June 1979.

Bitumen separation and upgrading are described. Special reference is made to the behaviour of asphaltene fraction during the hot water separation and the thermal methods of upgrading. Projections can also be made of asphaltene behaviour during in-situ recovery techniques.

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41. THE IMPACT OF HEAVY CRUDE OILS ON REFINERY OPERATIONS

A.R. Johnson, C.F. Jones, and H.F. Uhlig

The future of Heavy Oils and Tar Sands, chapter 77, 1st international conference Alberta, Canada June 1979.

A general overview is presented of the processing technology available for upgrading heavy crudes and tar sands and the impact of processing heavy crudes at the refinery than at the point of production is considered. Two alternate cases are considered - one based on producing Alberta (Cold Lake) crude for processing in a conversion refinery and the other based on producing Venezualan heavy oil to be processed in a fuel oil refinery. Approximate refinery processing costs are developed, but no attempt has been made to optimise the upgrading/refinery processing system.

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HYDROCRACKING CATALYSTS - CATALYST ACTIVITY AND AGING

42. A COMPARATIVE STUDY OF Fe CATALYSTS, $ZnCl_2$ CATALYSTS AND $ZnCL_2$-PROMOTED Fe CATLAYSTS FOR HYDROCRACKING OF ATHABASCA BITUMEN
W.A.O. Herrmann, L.P. Mysak and K. Belinko
CANMET Research Report 77-50, Jan. 1970

Tests were carried out during thermal hydrocracking of Athabasca bitumen on certain catalysts produced from inexpensive raw materials. Two classes were investigated: iron catalysts (Class I) and zinc chloride-promoted catalysts (Class II). These experiments were carried out in a batch autoclave. The reaction temperature varied from 385°C to 455°C at an H_2 pressure of 13.8 MPa. Reaction times ranged from 30 to 210 minutes.
The products obtained by using these catalysts were analyzed and compared with those using two conventional catalysts and those with no catalyst. The highest conversion was achieved with an Fe-lignite catalyst. The next most active was found to be 100% $ZnCL_2$. The latter produced a smaller amount of HC gas and significantly less sulphur in the product, and may therefore be considered more desirable.

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43. SURFACE LAYERING WITHIN GRAINS OF ALUMINA SUPPORT; EFFECTS ON HYDROTREATING CATALYSTS
J.F. Kriz, M. Ternan and R.H. Packwood
Ind. Eng. Chem. Prod. Res. Dev. Vol. 17, No. 2, 1978

Previous studies on hydrocracking catalyst development alluded to a surface layering effect of catalytic material within the particles or grains of the alumina catalyst support. Evidence is presented that surface layering can occur during the preparation of hydrotreating catalysts. An enhancement of the surface layering effect was observed when larger particles of alumina monohydrate were used. In contrast, during the impregnation of the catalytic material into the alumina monohydrate, the presence of an excessive amount of acid promoted gelling of the alumina and tended to eliminate surface layering. The effect of surface layering on sulfur and nitrogen conversion was measured. Other variations in the catalyst support such as the type of alumina monohydrate had no effect on conversion.

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44. HYDROCRACKING BITUMEN DERIVED FROM OIL SANDS WITH SULPHIDED MoO_3-CoO CATALYSTS HAVING SUPPORTS OF VARYING COMPOSITION
P.M. Boorman, J.F. Kriz, J.R. Brown and M. Ternan
Energy Research Laboratories, Energy Mines and Resources Ottawa, Ontario K1A 0G1 Canada

Hydrocracking reactions were promoted by adding fluoride ions to the catalyst and inhibited by adding sodium ions. The amount of coke on the catalyst

increased with fluoride and decreased with sodium. These observations were explained in terms of the electron acceptor properties of fluoride ions (large electronegativity) and electron donor properties of sodium ions (small electronegativity) and also in terms of Bronsted surface acidity. For catalysts of identical composition, (A) missing the molybdenum and cobalt salts with the alumina gel and calcining before impregnating the fluoride (or sodium), produced better reaction results than when (B) the sequence positions of fluoride (or sodium) were interchanged with molybdenum and cobalt. X-ray photoelectron spectra of used catalysts indicated that the ratio of Mo-O bonding to Mo-S bonging was greater for sequence (A) than for sequence (B). This suggested that (A) produced greater dispersion of cobalt and molybdenum on the support. The improved dispersion may have been responsible for the superior reaction results obtained with (A).

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45. HYDROCRACKING HYDROCRABON FEEDSTOCKS: ASPECTS OF CATALYSIS RELATED TO FEEDSTOCK COKING TENDENCY
Kriz, J.F., Ternan, M.
9th Can. Symp. Catalysis Proc, Quebec, 30 Sept.-3 Oct. 1984.

The feestock coking tendency when hydrocracking heavy or residual oils was measured to test the effectiveness of different catalysts. Influence of catalysts on the feedstock coking tendency was found to depend strongly on catalysts functionality. The catalyst property providing stability through effective hydrogen transfer appears to be particularly important. Information on the catalytic lowering of feedstock coking tendencies should lead to improved hydrocracking technologies. (excerpt).

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46. HYDROCRACKING OF ATHABASCA BITUMEN WITH HOMOGENEOUS CATALYSTS
Ukegawa, K.
Bull. Nat. Res. Inst. Pollution & Resourcesm V 12, N 4, Mar 1983, p 1-9 (10)

Hydrocracking of Athabasca bitumen with homogeneous catalyst (Ni, Fe, CO and Sn) at temperatures between 710-790 degrees F, reaction time between 0-120 min. and 1000 psi of initial hydrogen pressure has been investigated. The experiments resulted in reducing the pentane-insolubles (PI) in the bitumen by the homogeneous catalyst. Ni-catalyst was the best among those four catalysts. At 60 min. of reaction time, 750 degrees F was the best temperature to reduce PI. Between two Ni-catalysts, the one prepared from 92 MOLP-NIO/NI(OH)2 was better for PI reduction than the one prepared from 100 MOLP-NI(OH)2. (Author abstract).

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47. BITUMEN HYDROPROCESSING : EFFECTS OF METAL LOADING AND PROMOTERS IN MO-AL2O3 CATALYTIC SYSTEMS
Kriz, J.F.
Can J. Chem Eng. V 61, N 1, Feb 1983, p 68-72 (5)

Athabasca bitumen and a heavy gas oil (345-525 degrees C) derived from it were used in a high-pressure continuous flow system to evaluate catalytic effects of metal loading in hydroprocessing and to assess the role of promoters represented here by cobalt and sodium. A method that can be used for analysis of these effects is suggested. The two feestocks are compared in view of the expected catalyst performance and requirements in each case. It was found that desirable effects of promoters were greatest at low temperatures and with catalyst having low total metal loading. Desirable effects of catalysts having high molybdenum loading were intensified with increasing temperatures. These trends were similar with both feedstocks but the effects were much less pronounced with bitumen than with the gas oil. The need for an effective hydrogenation component was identified (author abstract).

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48. SOME EFFECTS OF CATALYST COMPOSITION ON DEACTIVATION AND COKE FORMATION WHEN HYDROCRACKING ATHABASCA BITUMEN
Ternan M., Kriz J.F.
Stud Surf Sci Catal, V 6, 1980, p 283-293 (11)

Catalyst coke formation, metal accumulation and rates of hydrocracking catalyst deactivation have been measured. The ranking of hydrocracking catalysts with different chemical compositions was considered in terms of electronic concepts. Initial catalyst deactivation rates for times on stream less than 50 hours were related to the initial catalyst coke content. For longer times on stream all catalyst regardless of their chemical composition had similar deactivation rates. A simple model of catalyst decay was developed and applied to data. The results indicated that catalyst chemical composition does not influence the long term deactivation rate, although it has a strong influence on most rates of reaction. An alternative strategy for more gradual deactivation is proposed. (author abstract)

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49. 4313818 - PATENT - U.S. HYDROCRACKING PROCESS UTILIZING HIGH SURFACE AREA CATALYSTS
Aldrige, C.L., Bearden-Jr., R.
Exxon Research and Engineering Co., Feb. 2, 1982 (11)

The patent covers a hydrocracking process which utilizes high surface area metal-containing catalysts. The catalyst is prepared using hydrocarbonaceous oil charge-stock having a Conradson carbon content of up to above 50 weight percent. The hydrocarbon oils include oils derived from oil shale, oil sands and coal liquefaction. A thermally decompossable metal compound is added to the hydrocarbon oil charge stock. The compound is heated in the presence of gas comprising of hydrogen and hydrogen sulfide to form a solid high surface area catalyst. 9 references

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50. 4295995 PATENT- U.S. CATALYSTS FOR HYDROCARBON TREATING PROCESSES
Bearden-Jr. R., Aldridge, C.L.
Exxon Research and Engineering Co., Oct. 20, 1981, (9)

The invention deals with a catalyst which can be used in treating hydrocarbonaceous oils derived from oil shale, oil sands and coal. Hydrocarbon treating processes include hydrocracking, catalytic cracking, and hydrodesulphurization. The patent covers both the method of preparing the catalyst and its use in hydrocarbon treating and conversion. The catalyst is composed of a catalytically active metal component, carbon and hydrogen deposited on a low surface area metal support. The preferred metal for the support is iron. The catalyst is particularly suitable for treating slurries.

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51. 4295996 PATENT - U.S. CATALYSTS FOR HYDROCARBON TREATING PROCESSES
Bearden-Jr. R., Aldridge, C.L., Pine L.A.
Exxon Research and Engineering Co., Oct. 20, 1981 (7)

The invention deals with a catalyst which can be used in treating hydrocarbonaceous oils derived from oil shale, oil sands and coal. It covers both its method of preparation and is use in hydrocarbon treating and conversion. The catalyst is composed of a catalytically active metal component, carbon and hydrogen deposited on a support which is an aluminum alloy powder.

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52. THE EFFECTS OF PORE SIZE IN MoO3-CoO-Al_2O_3 HYDROCRACKING CATALYSTS
Hardin, A.H., Ternan, M., Packwood, R.H.
Energy Mines and Resources Canada, CANMET Report 81-4E, Aug. 1981 (40)

Effects of pore size variations on hydrodesulphurization, hydrodenitrogenation, pitch conversion and coke formation were determined. The results indicated maxima for mass percent sulphur removal for pores near 15 NM for two catalyst. As well, the rates per unit area for S and N removal increased as mean pore diameters increased to about 50 NM, after which the rates appear to be constant. (excerpt).

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53. PREPARATION OF HIGH POROSITY CATALYSTS
Ternan, M., Packwood, R.H., Buchanan, R.M., Parsons, B.I.
Can J. Chem. Eng., V. 60, Feb 1982, p 33-39 (7)

Porous alumina catalysts having both large pore volume and surface area, were prepared. They were obtained from dilute alumina gels having large concentrations of acid and very large concentrations of fluid. Attempts were made to dry the gel without collapsing the pore structure between the alumina

particles. The catalysts were characterized by gravimetrical BET surface area, mercury porosimetry, X-ray diffraction and scanning electron microscopy. Catalyst supports having these geometric properties should eliminate mass transfer restrictions during hydrocracking of petroleum residua, heavy oils and bitumen derived from oil sand deposits. (excerpt).

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54. 4255253 PATENT - U.S. HYDROGEN PROCESSING OF HYDROCARBON FEEDS USING COATED CATALYSTS
Herrington, D.R., Schwerki, A.P., Dolhyj, S.R., Shaw, W.G.
Standared Oil Co., March 10, 1981 (6)

Catalysts consisting of a base support having a strongly adherent outer coating of an active catalytic material have been found to give superior results in known hydrogen processing reactions wherein sulfur, nitrogen and the metal content of a hydrogen feestock are reduced.

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55. 4214977 PATENT - U.S. HYDROCRACKING OF HEAVY OILS USING IRON COAL CATALYST
Ranganathan, R., Denis, J.M., Pruden, B.B.
Canada Energy Mines and Resources, July 29, 1980, (6)

A catalytic hydrocracking process in which the feed is mixed with iron-coal catalyst particles to form a slurry, which is hydrocracked in a tubular reactor. Coke formation inside the reactor is greatly reduced when this catalyst is used. 4 references.

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56. HYDROCRACKING ATHABASCA BITUMEN WITH ALKALI METAL PROMOTED CoO-Mo03-A1203 CATALYSTS
Kelly, J.F., Ternan, M.
Can J. Chem. Eng. V. 57, Dec. 1979, p 726-733 (8)

Alkali metal promoters (lithium, sodium and potassium) were added to catalysts used to hydrocrack Athabasca bitumen, in order to decrease the coke deposition which causes catalyst deactivation. Sodium and potassium promoters decreased the catalyst coke content, the catalyst surface area, and the pitch, oxygen, sulphur and nitrogen conversion. On a unit surface area basis, the sodium and potassium promoters increased the pitch and oxygen removal reaction rates. For all the lithium promoted catalysts both conversion and pitch, oxygen, sulphur and nitrogen removals decreased with increasing potassium content. The results are explained in terms of the changes in catalyst electronic properties caused by the addition of the promoters.

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57. DEVELOPMENT OF A SIMULATED CATALYST AGING TECHNIQUE
Kriz, J.F., Ternan, M.
Energy Mines and Resources Canada, Canmet Report 78-24, June 1978 (20)

A technique to simulate catalyst aging was developed whereby catalyst deactivation is accelerated by changing the operating conditions. Because of greatly accelerated aging, the technique can provide preliminary information on aging rates in a much shorter time than is normally required for performing an actual aging test. This report documents a series of tests performed to investigate the effect of variations in space velocity and temperature. Suitable deactivation conditions were found to prevail when both the space velocity and temperature were increased. In one particular case, this increase accelerated the aging rate about thirty times. The relationship between the aging patterns observed under simulated and actual aging conditions is discussed. An approximate quantitative link was established which provided an estimate of the catalyst aging rate from tests performed at simulated conditions. (author abstract).

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58. EFFECTS OF MEDIAN PORE DIAMETERS IN Co/Mo/AL203 CATALYSTS ON THE CONVERSION OF ATHABASCA BITUMEN
Hardin, A.H., Packwood, R.H., Ternan, M.
Am. Chem. Soc. Div Pet. Chem. Prepr, V. 23, N 4, Sept 1978, p 1450-1461 (12)

In order to determine the effects of catalyst physical parameters on hydrotreating and hydrocracking of Athabasca bitumen, a series of catalysts with varying surface areas, pore volumes, and mediam pore diameters was tested. Pore size effects on sulfur removal, nitrogen removal, metals removal, catalyst coke level, catalyst metal profile and product composition were determined.

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59. CHEMISTRY OF IRON SULPHATE-COAL CATALYSTS EMPLOYED IN THE HYDROCRACKING OF BITUMEN
Patmore, D.L., Pruden, B.B.
Energy, Mines and Resources Canada, CANMET Report ERP/ERL 77-72(TR), Sept. 1977 (20)

This study focused on the chemistry of iron during the thermal hydrocracking of Athabasca bitumen and heavy oils. Reports in the literature and an analysis of the reaction equilibria indicated that FeS is the stable phase of iron present during the hydrocracking process. The roles of particulate solid matter in decreasing coke deposition and thus reactor fouling and of iron containing catalysts in hydrocracking processes, are discussed.

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60. CATALYTIC HYDROCRACKING OF ATHABASCA BITUMEN IN A FLUIDIZED BED REACTOR - EFFECT OF PRESSURE ON CATALYST DECAY
Ranganathan, R., Logie, R.B., Denis, J.M.
Energy Mines and Resources Canada, CANMET Report 77-40, Nov. 1976 (26)

The effect of pressure on catalyst deactivation rate in a fluidized-bed reactor during the hydrocracking of Athabasca bitumen was studied. Two stages of deactivation were observed: an initial rapid stage, the rate of which was pressure-independent and which was apparantely due to the formation of a shell on the exterior of the catalyst particles by coke, metals and mineral matter deposition; followed by a slow stage, the rate of which decreased with increasing pressure. An empirical model was fitted to the increase in sulfur content of the products, which served as a measure of catalyst decay; the rapid stage was described by an exponential equation and the slow stage by a linear equation. Fluidized- and fixed-bed reactors were discussed, and it was pointed out that fluidized beds can continually remove and add catalyst thus making continuous catalyst replacement possible.

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61. A COMPARATIVE STUDY OF Fe CATALYSTS, $ZnCl_2$ CATALYST AND ZnCL2 - PROMOTED Fe CATALYSTS FOR HYDROCRACKING OF ATHABASCA BITUMEN
Belinko, K., Herrmann, W.A.O., Mysak, L.P.
Energy Mines and Resources Canada, CANMET Report 77-50, Jan. 1977 (24)

The catalytic activities of various Canadian raw materials are evaluated in the hydrocracking of Athabasca bitumen. These materials belonged to one of two classes, Fe-based catalysts of $ZnCl_2$-promoted Fe catalyst and were compared to 100 percent $ZnCl_2$ and other conventional catalysts. Performance assessment was based on the following criteria: yield of total liquid product boiling above 40 degrees C, percentage of residue boiling above 418 degrees C, analysis of high boiling residue by Conradson carbon formation and degree of hydrogenation in kerosen fraction. The most active catalyst was found to be Fe-lignite although 100 percent $ZnCl_2$ affords definite advantages.

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3 CATALYST SELECTION

The selection of the catalysts for the upgrading of pitch with methanol was based on a critical examination of the physical, chemical and catalytic properties of the catalysts in relation to the complex nature of pitch.

Catalytic hydrocracking processes utilise dual function catalysts, with one catalytic function to enhance the cracking of the high molecular species into smaller fragments and the other to hydrogenate the unstable fragments and thus prevent polymerisation. Since bond cracking reactions accelerate in the presence of a catalyst or with increasing temperature, sufficient hydrogen partial pressure and rapid hydrogen transfer is necessary in order to stabilise the unstable cracked intermediates which will, otherwise lead to the formation of coke. The hydrogenation function of the catalyst is thus, of key importance to the stability of an upgrading process.

Since the reactions which are catalysed by solid catalysts take place at the surface through the processes of adsorption and desorption, the rate of hydrogen transfer becomes a function of the effective catalyst area. Commercial catalysts with large surface areas are porous materials and before catalysis can take place the reactants have to diffuse through the pores of the catalyst. In the upgrading of pitch, the porosity of the catalyst becomes important because of possible mass transfer limitations of the asphaltene micelles in the pore system of the catalyst. Asphaltenes are high average molecular masses and contain relatively high concentrations of geometrically polycyclic aromatic structures.

Pitch also contains large concentrations of known catalyst poisons, such as the heteroatoms sulphur and nitrogen and the metals nickel, vanadium and iron. The tolerance of the catalysts to these poisons is essential to the performance of the hydrocracking catalysts.

In selecting the catalysts to be used in this testing program we have considered the following criteria:

- activity for decomposition of the methanol into hydrogen and carbon monoxide.
- activity for hydrocracking of the high moleculer species such as asphaltenes.
- enhanced hydrogen transfer activity
- preventing the coke formation at the reaction conditions
- tolerance to poisons known to be present in the pitch such as sulphur and nitrogen contained in high molecular compounds and heavy atoms (metals).

The catalytic properties as well as the physical properties of the supports and their tolerance to poisons were used for the catalyst selection.

Based on the literature data and previous experience it was decided early in the program to test molybdenum based catalysts for the function of hydrogen transfer and hydrocracking, iron based catalysts for their combined hydrocracking and coke prevention function and for the decomposition of the methanol it was selected to use zinc chromium catalysts generally used for methanol synthesis from synthesis gas.

The following catalysts were selected for the screening tests:

- red mud, an iron oxide concentrated by-product of the "aluminum extraction process. In support of the idea of a disposable inexpensive catalysts - two initial tests were carried out using "red mud" - an additive sometimes used in coal liquefaction with good results for hydrocracking and coke prevention.

- AERO HDS 1442-A ($CoO-MoO_3/Al_2O_3$) a commercial hydrocracking, hydro desulphurization catalyst. The Cobalt-Molybdenum on Alumina or Silica-Alumina catalysts enhance the hydrocracking and hydrogenation reactions and are believed to decompose methanol into hydrogen and carbon monoxide. The hydrogenation activity is provided by the metals molybdenum and cobalt and the hydrocracking activity by the alumina or alumina-silica supports. These catalysts are, also, tolerant to sulphur and nitrogen poisoning.

- C70-2 ($ZnO-Cr_2O_3$) - a "methanol synthesis" catalyst known to be effective in water gas shift reaction and believed to be also active for hydrogen transfer.
- Molybdenum hexacarbonyl - was selected on the basis of being a homogenous catalyst and thus without great access limitations and also known to be insensitive to heteroatom poisoning.

Santech prepared in house two catalysts using an inert microspherical support (Cab-O-Sil) with the objective of providing large pore-like structures which would allow the access of asphaltenic species to the active sites and thus enhance the hydrocracking - hydrogen transfer process. $FeSO_4$ and CoO/MoO_3 were the catalytic agents deposited on Cab-O-Sil.

The properties of the Cab-O-Sil support are given in appendix B. The active metals were supported on Cab-O-Sil. The advantage of the Cab-O-Sil support is that it provides a large surface area with a large pore structure. The large pore sturcture minimises the mass transfer limitations of the asphaltene malecules.

At the request of the scientific authority two catalysts were added to the list, They are designated as "MAP" and ZSM-5.

The catalysts detailed physical and chemical properties are given in appendix B.

4. TESTING PROGRAM

The objectives of the testing program carried out by Santech for this contract included catalyst screening and investigation of the effect of the reaction parameters upon the pitch conversion. These objectives were developed in a series of 24 (twenty four) test:

The Table 1 shows the catalysts and the range of variation for the reaction parameters investigated.

The reaction temperature was varied in the range of 370°C to 425°C, the reaction time from 60 to 240 minutes, the methanol/pitch ratio between 0.9 and 3.6. Two tests were carried out in presence of water in an attempt to enhance hydrogen formation and to reduce coke formation.

The results obtained in these tests will be discussed in the sections 4.5.

4.1 Description of Equipment

Testing was carried out, batchwise, in a hot charge/hot discharge stirred reactor. A schematic diagram of the apparatus used is shown in Figure 1.

The apparatus consists of a pitch/catalyst injection system, the reactor, a hot discharge receiver and a vapour phase recovery unit.

The reactor was a 2-litre, 316 stainless steel, magne-drive stirred, electrically heated autoclave. The maximum operating pressure and temperature of the reactor were 34.5 MPa and 450°C respectively.

For the present experimental program this reactor was equipped with the following features:

- An Autoclave Engineers Magnedrive II, variable speed, magnetically actuated, packless impeller system.
- Three internal baffles for increased mixing.
- Connections for pitch/catalyst slurry injection, gas inlet/outlet, thermocouple insertion and bottom discharge.
- Two thermocouples, connected to on/off controllers, dial temperature indicators and a multi-point recorder. One of the thermocouples was located in the reacting slurry and was used for controlling the heater and the other thermocouple was located on the outside reactor wall, and activated the heater shut-off at a preset temperature.
- Two electrical band heaters, 1500 watts each fitted around the reactor.

- A Bourdon-type dial pressure gauge, 0-35 MPa dial range with 0.5 MPa dial sub-divisions.

The hot discharge receiver was a custom-made 300 ml, 316 stainless steel, high pressure vessel. This vessel was provided with electrical band heaters and temperature measurement and control.

The pitch/catalyst injection system was in-house designed and included a hydraulic cylinder, 900 ml capacity, 34.5 MPa maximum operating pressure and 120°C maximum operating temperature. This cylinder was connected to a high pressure, 316 stainless steel, vessel. This vessel, designated the "hydraulic vessel", contained hydraulic oil and was connected to the inert gas manifold. The pitch/catalyst slurry drawn into the cylinder was injected into the reactor by applying in the "hydraulic vessel", an inert gas pressure higher than the pressure in the reactor.

The vapour phase recovery unit consisted of a tubular water condenser, a light liquid receiver, a refrigerated trap, a gas sampling arrangement and a wet-test gas meter. The off gas was discharged via a scrubbing tower. The light condensed liquid receiver was a 1-litre, 316 stainless steel, high pressure vessel

The refrigerated liquid trap was a 300 ml capacity, 316 stainless steel vessel with a cooling mantle.

The gas sampling arrangement allowed thorough purging of the gas sampler tube before a sample was taken.

The wet-test gas meter was a "Precision Scientic", model 63126, 3.0 litres dial range with 0.01 litres dial sub-divisions.

4.2. Description of Procedures

4.2.1 Testing Procedure

The unit was pressure tested to 1.5 times the reaction pressure with inert gas (He/N_2) before each test.

The methanol or methanol/water mixtures, weighed to the nearest 0.1 g, were charged into the reactor at room temperature by suction under a slight vacuum.

The reactor was then heated, gradually under constant mixing to the desired reaction temperature. Both the inside and outside temperatures of reactor were continuously recorded. The pressure in the reactor which was constantly rising during the heat-up and reaction time periods, was recorded at regular intervals.

The pitch/catalyst slurry was prepared by mixing pre-weighed amounts of pitch and catalyst to the desired pitch/catalyst ratio and it was then heated to a temperature at which the slurry had sufficient fluidity for injection, (normally between 150 and 170°C).

The prepared slurry was drawn into the hydraulic cylinder, which was kept at 100°C, and immediately injected into the reactor, when the reactor inside temperature reached 150°C.

During the length of the reaction time, the temperature of the reactants was maintained constant and the pressure in the reactor was maintained below 30.3 MPa. The reactor pressure control was achieved in tests Nos. 3-12 by a back pressure regulator installed in the line connecting the reactor to the vapour phase recovery unit.

Vapour from the reactor was released into the vapour phase recovery unit when the pressure in the reactor exceeded the pre-adjusted set-point of the back pressure regulator. In test Nos. 13-24, the back pressure regulator was replaced by a manual valve. The pressure was manually controlled by reducing the presure in the reactor from 30.3 to 25.5 MPa when the pressure in the reactor reached 30.3 MPa.

In all tests the vapour released into the vapour phase recovery unit was cooled in the water condenser, the liquid products condensed from the vapour phase were collected in the liquid receiver and liquid trap and the non-condensible gases were metered on the wet-test meter before being discharged.

Samples of the non-condensible gases were taken during the course of the reaction time and analyzed by gas chromatography. The time at which a gas sample was taken was recorded and the liquids collected in the liquid receiver and liquid trap, were recovered and weighed separately from the products collected at the end of the test.

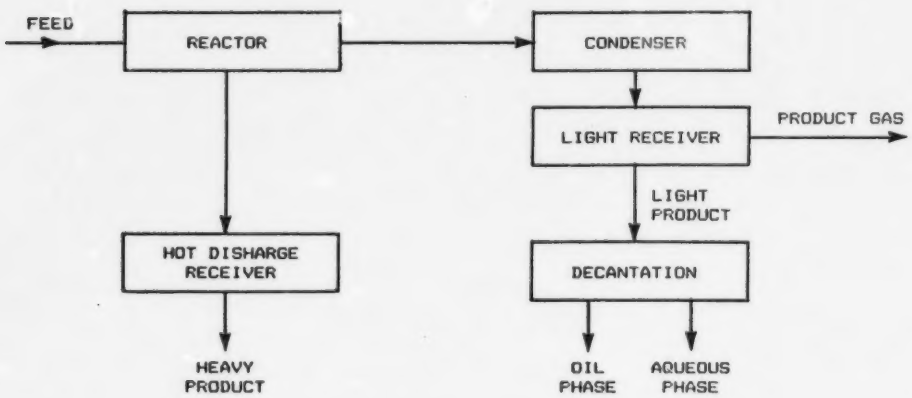
Upon completion of the reaction time, the liquid-solid product of the reaction was discharged in the hot discharge receiver which was kept at 250°C to maintain the fluidity of the liuqid-solid product. The final vapour phase was vented through the vapour phase recovery unit and the non-condensible gases were metered on the wet-test meter and analyzed by gas chromatography. The condensed liquids collected in the liquid receiver and liquid trap were recovered, weighed and analyzed.

The liquid-slurry product discharged in the hot discharge receiver was recovered weighed and analysed.

The reactor and hot discharge receiver were allowed to cool to room temperature. Both vessels were then washed with THF to recover the solid-liquid product which remained in the vessels. The liquid-solid product carried in THF was recoverd from the THF in a rotary vacuum evaporator. The weight of this product, designated "washings", was used in the calculation of the material balance.

4.2.2 Product Recovery

The products were recovered in three streams, as shown in the following diagram.



The product collected in the hot discharge receiver was recovered at the completion of the test. This product, designated "heavy product", contained the catalyst and was a solid at room temperature.

The vapour phase products were recovered in two streams: the light liquid stream and the non-condensible gas stream. The light product stream recovered from the liquid receiver, contained methanol, water and organic liquids formed during the reaction. This stream consisted of two different layers. The layers were separated by decantation. The top oil-like layer was designated the "oil phase" and the bottom water-like layer was designated the "aqueous phase".

The non-condensible gas stream was recovered by measuring the volume of the gases on a wet-test meter and analyzing the gas sample by gas chromatography. This stream composed of H_2, CO_2, CO, H_2S, CH_4, C_2H_6, C_3H_8, C_4H_{10} and dimethyl ether. Depending on the amount of methanol charged into the cold reactor and on the type of catalyst used, light and non-condensible gases product streams were recovered several times during the duration of the reaction as a result of releasing vapour from the reactor into the vapour phase recovery unit in order to control the pressure in the reactor.

Two tests were carried out in duplicate in order to test the reproductibility of the results (respectively 14/16 and 18/19).

In test No.5 the catalyst was separated from the heavy product by filtration. In this test the reactor, upon completion of the reaction time, was allowed to cool to 250°C. The final vapour phase was then released into the vapour phase recovery unit and collected as described above. The reactor was subsequently pressurised with inert gas at 345 KPa and the liquid/solid product was transfered into a pressure filter holder, which was connected to the reactor and was maintained at 250°C. The filtration rate, however, was very slow and the final cake obtained contained a large percentage of the heavy product soluble material.

4.2.3 Material Balance Calculation

The material balance was calculated as percent of total input.

The weight of pitch/catalyst slurry introduced was obtained by difference of the weight of the container before the slurry injection less the weight of the container after the injection of the slurry in the reactor and drainage of the lines back into the initial container.

The weight of methanol introduced was obtained in the same way. Methanol being a material with very high vapour pressure at room temperature, the handling of the container was given additional care to minimize losses by evaporation.

The output was calculated by summing the weights of the heavy product, light stream collected in the liquid receiver, light condensate collected in the ice trap, washings (after the solvent was removed by evaporation) and of the non condensible gases. The later was calculated from the STP volume of the gases and the chromatographic analysis.

The Table 2 presents the material balance calculations for all the tests.

Generally the calculations resulted in material balances lower than 100%. The reasons may be composite losses in the handling of methanol and/or of the light product from the liquid receiver and light condensate from the trap. Also errors in the chromatographic analysis may result in lower results for the non condensible gases.

Tests resulting in material balances lower than 95% were not reported.

4.2.4 Products Analysis

The product streams were separately analysed. The analytical procedures used are outlined in detail in Appendix A.

The heavy product, including the catalyst, was analysed for selective solvent extraction with heptane, toluene and tetrahydrofuran (THF) to determine the maltene, asphaltenes, pre-asphaltenes and solids. Table 4 represents the percent weights of heptane, toluene and THF insolubles content in the heavy product of each test. The percent weight of maltenes, asphaltenes, preasphaltenes and solids in the product, based on the pitch feeds, are shown in table 5.

A representative, homogeneous sample of the heavy product was subjected to vacuum distillation under 0.1 mmHg vacuum to 525^{o}C (equivalent atmospheric pressure boiling point) or until cracking occurred. The percent weight of the heavy product distillate fractions for each test is given in table 5.

The distillation residue of the heavy product was analysed for sulphur, ash and CHN content. The results of the ultimate analysis are shown in table 6.

4.2.5 Catalyst Preparation

Santech undertook the preparation of two catalysts. For both these catalysts, Cab-O-Sil was used as support and the active catalytic agents were deposited on the surface of the Cab-O-Sil microspheres.
The chemical composition, physical properties and structure of Cab-O-Sil are given in Appendix B.

A pre-determined weight of Cab-O-sil was impregnated with a solution of pre-determined concentration, containing salts of the desired active metals.

The impregnation resulted in a free flowing, homogeneous paste which was dried in air at 150^{o}C for 7 hours. The dried material was then calcined at 400^{o}C for 6 hours.

The two catalysts prepared were designated "$FeSO_4$/Cab-O-Sil" and "CoMo/Cab-O-sil".

The materials and the weights used to prepare the catalysts are shown below:

FeSO4/Cab-O-Sil Catalyst

Support	:	Cab-O-Sil	179.1 (g)
Impregnating Solution:		$FeSO_4.7H_2O$	311.0 (g)
		Distilled Water	950.0 (g)

CoMo/Cab-O-Sil Catalyst

Support	:	Cab-O-Sil	390.3 (g)
Impregnating Solution:		$(NH_4)_6(Mo_7O_{24}).4H_2O$	115.0 (g)
		$Co(NO_3)_2 6H_2O$	61.9 (g)
		Distilled Water	3,914.0 (g)

The content of active metals in the prepared catalysts, obtained by atomic absorption analysis, based on the total weight of the catalyst are presented below.

$FeSO_4$/Cab-O-Sil	Fe	18.4% wt
CoMo/Cab-O-Sil	Mo	12.4 % wt
	Co	2.3 % wt

The AERO HDS-1442A catalyst was presulphided in tests No. 3 and 16. The presulphiding of the catalyst was carried out in a flow of 5% vol H_2S in H_2, using the procedure recommended by the manufacturers of the catalyst.

4.3. Feed Characterization

The pitch utilized as feed was supplied by CANMET,

Table 15 presents its characteristics

4.4 Catalyst Screening

The catalyst screening tests were carried out at 400°C and 120 min using fresh catalyst for each test. The catalysts effectiveness was evaluated on the basis of the pitch conversion into distillates. The six commercial catalysts and the two in-house prepared catalysts tested are listed in table 16.

The Cobalt, Molybdenum catalyst AERO HDS 1442A was presulphided prior to being used in tests 3 and 16, and it was used, without pretreatment in the tests 7, 12, 13, 14, 15 and 17.

The similarity of the results obtained in the duplicate tests No. 14 and 16, indicates that the presulphiding of the HDS-1442A catalyst in test No. 16 had no significant effect on pitch conversion, distillate yield and product distribution. It is possible, however, that the catalyst is sulphided at the reaction conditions during the reaction time due to the high content of sulphur in the pitch, which make the presulphiding unnecessary.

The most effective catalyst for pitch conversion, distillate yield and product distribution was the CoMo-Cab-O-Sil used in test No. 19 (duplicate test No. 18) at 380°C and 120 minutes reaction time. As shown in table 17, the pitch conversion and distillate yield obtained in this test were 68.4% wt. and 64.8% wt. of the pitch feed respectively. From table 4 and figure 2 it can be seen that the formation of coke was negligible in this test.

The performance of the AERO HDS-1442A catalyst, under similar conditions as those of test No. 19, was somewhat lower than the CoMo-Cab-O-Sil catalyst. In test No. 3, using the HDS-1442A catalyst, at 385°C and 120 minutes reaction time, the pitch conversion and distillate yield were 61.1% wt. and 54.5% wt. of the pitch feed respectively.

All the other catalysts tested resulted in lower pitch conversions (less than 50% wt.) and lower distillate yields as shown in table 17. The lowest pitch conversion (26.8% wt.) was obtained with the H-ZSM-5 catalyst, in test No. 22, at 375°C and 120 minutes reaction time.

The formation of coke during the reaction time appeared to be function of the temperature and type of catalyst. From table 18, it can be seen that the content of coke was relatively high in the product of the tests with the $FeSO_4$-Cab-O-Sil, M.A.P., C70-2/HDS-1442A, C70-2/M.A.P. and the red mud catalysts. The content of coke was negligible in the product of the tests with the Molybdenum hexacarbonyl and H-ZSM-5 catalysts.

The extent of methanol decomposition and the concentration of gases formed during the reaction time varied considerably for each catalyst as shown in tables, No. 10 to 13. The predominant gases formed in all tests were hydrogen, carbon dioxide, methane and dimethyl ether.

The Zinc, Chromium catalyst (C70-2) appeared to have the highest selectivity in decomposing the methanol into hydrogen and carbon monoxide as shown in table 12 and figures 15 and 16. The H_2 concentration in the gaseous phase analysed during tests 4 and 9 remained above 25% for the whole duration of the tests.

The lowest decomposition of methanol into H_2 and CO was observed in test No. 21 with the H-ZSM-5 catalyst, as shown in table 13 and figure 19. In this test, the gas sample at the onset of the reaction contained mainly dimethyl ether (96 Vol%).

A similar pattern of behaviour of the gas composition evolution was observed in all the tests with HDS-1442A, $Mo(CO)_6$ and CoMo-Cab-O-Sil Catalysts, as shown in tables 10, 11, 12 and figures 5 to 14. In these tests the concentration of hydrogen decreased with reaction time and the concentration of dimethyl ether decrease with reaction time in favour of methane and carbon dioxide formation.

The decrease in the concentration of dimethyl ether with reaction time in favour of carbon dioxide and methane was observed in all tests.

The conversion of pitch, the distillate yield and the consumption of methanol obtained in each test are shown in table 17. The distribution of the product, i.e. atmospheric distillate, vacuum distillate, non-distillable and the THF insolubles, obtained in each test are given in table 18.

4.5 Investigation of Experimental Parameters

4.5.1 Temperature Effect

The effect of temperature was investigated in the range of 300°C to 425°C using as catalysts, the Red Mud (iron oxide) and the AERO HDS-1442A.

Tests No. 1 and No. 2 wer conducted at 300°C and 400°C respectively using the iron oxide catalyst, 120 minutes reaction time, and similar ratios of pitch/catalyst and methanol/pitch. In test No. 1 the decomposition of methanol and the hydrocracking of the pitch at 300°C appeared to be negligible. In this test the light stream collected at the end of the 120 minutes reaction time was practically all methanol with insignificants amounts of organic oil and water. The weight of methanol recovered in the light stream was about the same as the weight of the methanol charged into the reactor. The heavy product stream collected in this test was non-distillable and the weight content of oils, asphaltenes, pre-asphaltenes and solids, determined by selective solvent extraction were similar to those of the pitch feed as shown in tables 15 and 4. The results obtained at higher temperature indicated the inability of the iron oxide catalyst to prevent retrogressive reactions of the asphaltenes due probably to a very low hydrogen partial pressure. The formation of coke was very high. As shown in table 4, 31.1 wt % of the feed pitch was mainly converted into coke. Because of the high content of coke the heavy product solidified in the hot discharge receiver and lines after it was transfered from the reactor into the hot discharge receiver. The material balance was 90.0 wt % due to losses, in recovering the heavy product.

The AERO HDS-1442A catalyst was tested at four temperatures in the range 370-425°C. Tests No. 17, 3, 16 and 12 were conducted at 370, 385, 400 and 425°C respectively.

The highest pitch conversion, and distillate yield and the least coke formation were obtained at the lower end of the temperature range tested, as shown in tables 17, 18 and figure 3.

The pitch conversion and the distillate yield decreased with increasing temperature, while the formation of coke increased considerably. In the 425°C test, 46.4 wt% of the pitch feed was converted into coke. (Test No.12)

The Aqueous phase of the light product was analysed by gas chromatography to determine the contents of unreacted methanol and water. The percent weight content of methanol and water in the aqueous phase of the light products are presented in table 7. The term "others" in this table represents the unidentifiable materials which shown in the chromatographic analysis. Because of the small concentration of these materials in the light product the identification of these materials was not attempted. The weights of methanol, water and organic oil in the light product of each test are given in table 8.
The oil phase of the light product was analysed by simulated distillation. The percent weight of the simulated distillation for all tests are given in table 9. The non-condensible gases stream was analysed on a "Carle" gas chromatograph to determine the percentage volume of H_2, CO_2, CO, C_1, C_2, C_3, and C_4 hydrocarbons, and dimethyl ether.

The volumetric composition of the gas samples are shown in table 10 for the tests with the AERO HDS-1442A catalyst, in table 11 for the tests with the CoMo-Cab-O-Sil catalyst, in table 12 for the tests with the C70-2 catalyst and in table 13 for the remaining catalyst.

The volumetric composition of each component in a gas sample is plotted against the reaction time for each test as shown in figures 5 to 21. In there figures, the straight lines drawn between the points of a gas component are only used for better visual identification of the gas sample components.

The C,H,N,S, content of the total distillable product was determined for test Nos 3, 10 and 18. The samples prepared for this analysis consisted of prorated amounts of the oil phase of the light product and the distillable fractions of the heavy product. Table 14 presents the percent weight content of C,H,N,S, for tests 3, 10 and 18.

4.5.2. Reaction Time Effect

The effect of the reaction time was investigated with the CoMo-Cab O Sil catalyst at 380°C and reactions times of 60, 120 and 240 minutes in tests Nos. 23, 19 and 24 respectively. The results obtained in these tests indicate as shown in table 18 and figure 4, that the highest pitch conversion and the highest distillate yield were obtained at the 120 minute reaction time test.

The pitch conversion in this test was 68.4 wt.% of the pitch feed and the distillate yield, was 62.7 wt.% of the pitch feed.

The 60 minute reation time test resulted in much lower pitch conversion and distillate yield, 36.4 wt.% pitch conversion and 31.3 wt% distillate yield.

The pitch conversion and distillate yield obtained at the 240 minute reaction time test were also lower, 53.7% wt pitch conversion and 46.7% distillate yield.

The results seem to suggest that pitch conversion in the presence of methanol is a somewhat slow process and to confirm a direct relationship to the hydrogen partial pressure. It appears that in batch mode, without the continuous methanol input and gas removal, the hydrogen partial pressure remains only for a limited time sufficiently high for the process to continue and this time appears to be around 120 minutes, after which it becomes insufficient for the hydrocracking to occur. Some thermal cracking does probably still continues resulting in retrogressive reactions.

At conditions of a continuous flow reactor where the hydrogen partial pressure can be maintained constant at higher levels, the results will probably be considerably better.

4.5.3. Addition of Water Effect

In an effort to find ways to reduce coke formation, we considered adding water to reaction mixture. The purpose of the water addition was to promote the water gas shift reaction. The effect of water addition was investigated in tests Nos. 7 and 9 using the HDS-1442A and C70-2 catalysts respectively. Both tests were conducted at 400°C, 120 minutes reaction time and a methanol/pitch ratio of 4.0. From table 17 and 18, the comparison of the results of test No. 7 with these of test No. 16, conducted under the same conditions but without the addition of water, indicate that the addition of water had no beneficial effect on pitch conversion, distillate yield and product distributions. Similarly, the comparison of the results of test No. 9 with those of test No. 4 indicate that the addition of water had no significant effect on pitch conversion and distillate yield, but it had a considerable effect, in this case, on the formation of coke. The test No. 9 product contained 19.9%wt. coke, in comparison to 4.6 wt%. coke in the product of the test No. 4.

These results suggest that the water presence led mainly to the deactivation of the catalyst.

4.5.4. Methanol/Pitch Ratio Effect

The theoretical consideration of this parameter suggests that a higher methanol/pitch ratio should influence favourably the pitch hydrocracking process due to the enhanced formation of hydrogen as well as to an increased supercritical solvent effect. At the conditions of batch testing though, it was difficult to assess these effects due to the limitations imposed by the equipment. In tests with methanol/pitch ratio greater than 1 the pressure in the reactor reached the maximum allowable operating pressure of the reactor before the reaction temperature was reached. In order to maintain the pressure in the reactor below the maximum operating pressure of the reactor, vapour was released into the vapour phase recovery unit. In the early stages of the reaction time, the liquid recovered from the released vapour phase was composed mainly of methanol. The amount of methanol was, thus, limited to about the same amount at the onset of the reaction time in all tests regardless of the initial methanol/pitch ratio.

In tests No.3 and 17 the methanol/pitch ratios used were 3.6 and 1.3 respectively. These two tests were carried out under similar experimental conditions with the exception of the methanol/pitch ratio.

From the results obtained at the conditions of testing, it appears that the effect of the methanol/pitch ratio would not be significant. As explained above, this might not be the true effect of the methanol/pitch ratio, but it may be due to the removal of methanol from the reaction system in order to maintain the reaction pressure below the maximum reactor operating pressure.

5. DISCUSSION OF THE EXPERIMENTAL RESULTS

5.1 General Considerations

The techniques used by Santech allowed for consistent results. The tests carried out for reproducibility control, namely, 14 vs 16 and 18 vs 19 showed good reproducibility of both reaction conditions and results as shown in tables 1, 17 and 18.

The material balances calculated for all tests reported are in excess of 95% which indicate a good control over the testing procedures and equipment.

The methanol decomposition was monitored during the test by the analysis of the gaseous phase during the reaction. The pitch conversion was calculated from the difference between the 525°C- fraction of the product and that of the feed which was entirely 525°C+.

It seems important to note that, due to the batch mode of testing, the methanol decomposition calculated for these tests exceeds many fold the necessary levels for the process to take place. The results indicate a rapid decomposition of the methanol into the hydrogen and dimethylether, followed by the slower but undesired process of methane formation from the dimethylether at the expense of hydrogen consumption and water production. In a continuous mode of processing the pitch with methanol, the reactor will be designed to allow for a rapid removal and quenching of the gaseous phase which will reduce considerably the methane formation. The DME could then be converted into gasoline over a ZSM5 zeolite catalyst or back into methanol. Any one of these routes will result in a considerable reduction of the methanol consumption per barrel of distilled product.

5.2 Pitch Conversion

The pitch conversion into distillate which was the main criterion for evaluation of the results obtained and it was calculated as the percent of feed pitch remained as 525°C+ fraction of the total product.

It should also be noted that the 525°C+ fraction of the product includes the THF insoluble coke formed by thermal cracking followed by polymerization and thus the value obtained for conversion is not absolute, but rather a practical measure of pitch conversion.

The highest pitch conversion was calculated for the tests using Cobalt, Molybdemun catalysts at a temperature not exceeding 380°C and 120 minutes reaction time.

These results suggest that the pitch conversion is the result of hydrocracking and that due to the rather low hydrogen partial pressure can be conducted only at the lower end of the hydrocracking temperature range (380°C) and consequently is a rather slow process. It is possible thus to speculate that the results of the process if it would be carried out in a continuous mode where the hydrogen partial pressure can be maintained constant and at higher levels, will more likely improve.

The better performance, achieved with the HDS-1442 A and the CoMo-Cab-O-Sil catalysts may be attributed to the pronounced hydrocracking and hydrogen transfer activities of these catalysts. The higher effectiveness obtained with the CoMo-Cab-O-Sil catalyst, as compared to that of the HDS-1442A catalyst, are probably due to the larger pore structure of CoMo-Cab-O-Sil catalyst.

Prior investigation of the effect of the pore size in the MoO_3-CoO/Al_2O_3 on the hydroprocessing of bitumen (58, 62) found that the bitumen conversion was limited by the rate of mass transfer in small pore catalysts and the catalyst effectiveness was increased with increasing pore size.

The low pitch conversion obtained with the H-ZSM-5 catalyst may be explained by mass transfer limitations of the large molecules and asphaltene micelles in the small pore structure of the zeolite catalyst.

The $FeSO_4$ - Cab-O-Sil and the CoMo-Cab-O-Sil catalysts were prepared using the same support. The performance, however, of $FeSO_4$ - Cab-O-Sil catalyst was inferior to that the CoMo-Cab-O-Sil catalyst. The formation of coke on the $FeSO_4$ - Cab O Sil catalyst indicates that this catalyst exhibited poor hydrogenation activity.

The poor performance of the ZnO-Cr_2O_3 catalyst was probably due to the high sensitivity of this catalyst towards sulphur poisoning.

The conversion obtained with the CoMo-Cab-O-Sil catalyst at 380°C and 120 minutes reaction time is comparable with the pitch conversions obtained in other commercially proven processes.

5.3 Distillate Quality and Yield

The results shown in tables 14, 17 and 18 suggest that under the effect of Co/Mo catalysts, at 380°C distillate yields in excess of 55% were consistently obtained. Generally, 22-27% of the initial pitch was converted into lighter distillates (atmospheric distillate cut is 350°C) with the balance being vacuum distillates.

Composite distillate samples of products from tests No. 3, 10 and 18 had H/C of 1.7 compared to only 1.3 in the feed. This may suggest that further upgrading of these products will be achieved readily and that marketable products can be obtained from pitch by this process.

6. PRELIMINARY ECONOMICS

Based on the preliminary results obtained in batch mode, Santech used an existing proprietary economic model to investigate the economic feasibility of the process.

The following assumptions were used in order to calculate an internal rate of return of investment (before tax).

- a 10,000 Bbl/day plant located in Alberta.
- the methanol will be produced in plant from natural gas.
- the crude oil bench reference price $27.50 US/bbl
- pitch priced on the basis of energy contained.
- rate of inflation 4%
- plant life 20 years
- debt amortization 20 years
- equity 60%

For these conditions, 5.1 bbl/tone of distillate hydrotreated product will be obtained. The capital cost including a contingency of 20% and the engineering and working capital as well as the start-up costs, was calculated at $225,067,000 US. The product revenue does not include the sale of sulphur or ammonia.

It was assumed that purchased natural gas will be used as inplant fuel. The internal rate of return calculated was 19.79%.

A sensitivity anmalysis of the model indicated that the critical variables are the rate of the methanol consumption, the price of the pitch and the distillate yield.

The results of the economic evaluation are shown in tables 19 to 22 and figures 22 to 25.

7. CONCLUSIONS

The experimental program carried out for thus contract was relatively limited in scope and budget. The main objective was to investigate the feasibility of the pitch upgrading using methanol and to identify the catalyst most suitable and the range of reaction conditions applicable.

The Molybdenum containing catalysts resulted in the highest pitch conversion to distillate.

Of the catalysts tested, the CoMo-Cab-O-Sil catalyst prepared in house by Santech gave the best results at 380 °C and 120 minuted reaction time. A pitch conversion of 68.4% wt. of the pitch feed was obtained with this catalyst without the formation of coke, (tables 17 and 18). An increase in the H/C ratio and a decrease in the N and S contents of the distillate product were achieved as shown in table. 14.

The catalysts known to be active in the methanol decomposition reaction did not result in high pitch conversion.

The addition of water resulted in deactivation of the catalysts and increased coke formation.

A direct correlation of the distillate yield to the hydrogen partial pressure was found in all tests.

The results obtained in this work indicate that the upgrading of pitch into distillate products using methanol as a hydrogen donor is a feasible process and it consitutes an alternative for upgrading of heavy stocks under certain conditions such as:

- when a hydrogen manufacturing facility is not available and transportation of liquid methanol instead of high pressure hydrogen is cheaper.
- for small plants at remote location
- when there is a surplus of low cost methanol available in the proximity of a heavy residue source.

TABLE 1
TESTING PROGRAM - REACTION CONDITIONS

CATALYST	TEST NR.	TEMP. (o C)	TIME (min)	MAX PRES. (psi)	PITCH CAT. RATIO	MEOH PITCH RATIO	MEOH H2O RATIO
HDS-1442-A	17	370	120	4000	6.7	1.3	
	3	395	120	4300	3.0	3.6	
	14	400	120	4100	3.3	1.4	
	16*	400	120	4300	3.4	1.3	
	12	425	120	4100	4.0	0.9	
	15	400	60	4100	3.0	1.5	
	7	400	120	3800	4.6	1.8	4.0
CoMo-CabOsil	23	380	60	4400	5.6	2.9	
	18	380	120	4300	5.6	2.8	
	19	380	120	4400	5.6	2.5	
	24	380	240	4450	5.6	2.7	
C70-2 (Zn-Cr)	4	400	120	4200	12.0	2.9	
	5	400	>120	4300	12.0	2.4	
	9	400	120	3800	12.0	1.7	4.0
Mo(CO)6	10	400	120	3400	6.0	1.7	
FeSO4-CabOsil	11	400	120	3900	4.4	1.2	
M.A.P.	20	375	120	4300	5.0	2.3	
H-ZSM-5	21	375	120	4000	7.8	2.7	
C70-2/HDS	13	400	120	4000	6.2	1.8	
Zn-Cr/M.A.P.	22	375	120	4400	5.0	2.6	
RED MUD	1	300	120	1320	10.0	1.0	
	2	400	120	2700	10.0	0.9	

* The catalyst was presulphided

TABLE 2 MATERIAL BALANCE

TEST NR.	INPUT PITCH g	MeOH g	H2O g	CATALYST g	TOTAL g	OUTPUT GAS g	HEAVY g	LIGHT g	TOTAL RECOVERY g	MATERIAL BALANCE %INPUT
3	154.5	558.5	0.0	51.5	764.5	282.8	135.9	314.0	732.7	96
4	207.3	610.9	0.0	17.3	835.5	209.1	170.0	435.8	814.9	98
5	210.1	510.0	0.0	17.5	737.6	152.4	203.1	363.5	719.0	97
6	100.6	213.2	118.4	63.1	495.3	101.5	112.1	266.5	480.1	97
7	219.2	397.8	99.2	47.9	764.1	117.9	186.3	434.9	739.1	97
9	231.9	400.0	100.0	19.3	751.2	147.9	184.2	408.2	740.3	99
10	232.6	401.5	0.0	38.5	672.6	213.1	166.7	290.9	670.7	100
11	241.5	280.0	0.0	55.0	576.5	123.8	226.0	202.2	552.0	96
12	264.0	250.0	0.0	66.7	580.7	139.2	208.0	210.3	557.5	96
13	219.7	400.0	0.0	35.7	655.4	215.6	173.1	259.4	648.1	99
14	282.5	400.0	0.0	86.8	769.3	194.5	257.2	283.0	734.7	96
15	264.1	400.0	0.0	88.0	752.1	171.8	274.6	272.6	719.0	96
16	299.7	399.0	0.0	87.5	786.2	229.8	265.8	266.9	762.5	97
17	316.0	400.0	0.0	47.4	763.4	219.2	334.3	169.7	723.2	95
18	193.5	540.0	0.0	34.7	768.2	205.5	173.9	364.2	743.6	97
19	215.9	550.0	0.0	38.7	804.6	174.0	199.1	397.1	770.2	96
20	235.7	550.0	0.0	47.3	833.0	77.4	231.7	486.6	795.7	96
21	206.5	550.0	0.0	26.4	782.9	125.6	189.6	434.4	749.6	96
22	228.2	600.0	0.0	45.6	873.8	136.6	230.2	472.0	838.8	96
23	203.6	600.0	0.0	36.5	840.1	141.7	184.4	480.3	806.4	96
24	222.8	595.0	0.0	39.9	857.7	223.5	173.1	433.4	830.0	97

TABLE 3

SOLVENT EXTRACTION ANALYSIS OF
HEAVY PRODUCT STREAM

CATALYST	TEST NR.	HEPTANE INSOL.	TOLUENE INSOL.	THF* INSOL. (INCL. CATALYST)	ASH IN THF INSOL.
HDS-1442-A	17	35.3%	20.0%	20.0%	
	3	64.7%	47.7%	43.9%	66.5%
	14	74.5%	55.9%	52.7%	
	16	70.4%	53.2%	48.3%	
	12	91.0%	91.0%	91.0%	
	15	68.7%	48.7%	46.8%	
	7	68.4%	48.7%	42.9%	
CoMo-CabOsil	23	42.3%	21.6%	20.0%	
	18	42.9%	26.0%	24.7%	
	19	45.8%	23.5%	22.5%	
	24	51.2%	29.2%	27.7%	
C70-2 (Zn-Cr)	4	56.4%	21.0%	15.8%	51.5%
	5	64.3%	39.7%	34.7%	23.7%
	9	60.5%	46.6%	35.5%	45.9%
Mo(CO)6	10	37.8%	13.2%	11.1%	
FeSO4-CabOsil	11	63.8%	49.9%	44.0%	42.0%
M.A.P.	20	67.1%	46.0%	45.4%	
H-ZSM-5	21	47.0%	17.1%	12.5%	
C70-2/HDS	13	65.9%	44.7%	38.3%	
Zn-Cr/M.A.P.	22	61.2%	41.7%	31.8%	
RED MUD	1	31.7%	10.6%	10.5%	
	2	68.8%	54.9%	46.3%	

NOTE: All figures are in % wt.

TABLE 4

LIQUID ORGANIC PRODUCT DISTRIBUTION
BY SOLVENT EXTRACTION*

(% WEIGHT OF THE PITCH FEED)

CATALYST	TEST NR.	OILS	ASPHAL.	PRE-ASPHAL.	SOLIDS
HDS-1442-A	17	75.2	16.2	0.0	6.2
	3	69.9	15.0	3.3	5.3
	14	60.8	16.9	2.9	17.3
	16	57.9	15.3	4.3	13.6
	12	34.9	0.0	0.0	46.4
	15	62.1	20.8	2.0	15.3
	7	60.6	16.7	4.9	14.6
CoMo-CabOsil	23	74.5	18.7	1.4	0.2
	18	78.7	15.2	1.2	4.3
	19	72.1	20.6	0.9	2.8
	24	71.1	17.1	1.2	3.6
C70-2 (Zn-Cr)	4	62.3	29.0	4.3	4.6
	5	46.4	23.8	4.8	25.2
	9	51.9	11.0	8.8	19.9
Mo(CO)6	10	78.2	17.6	1.5	.0
FeSO4-CabOsil	11	61.6	13.0	5.5	18.4
M.A.P.	20	51.0	20.7	0.6	24.6
H-ZSM-5	21	66.6	27.5	4.2	0.0
C70-2/HDS	13	65.3	16.7	5.0	13.9
Zn-Cr/M.A.P.	22	58.5	19.7	10.0	12.1
RED MUD	1	75.0	23.2	0.1	1.5
	2	27.1	12.1	7.5	30.1

* OILS = Heptane Solubles
ASPHLTENES = (Tol.-Hep.) Solubles
PRE-ASPHALTENESS=(THF-TOL.) Solubles
SOLIDS = THF Insolubles

TABLE 5.

VACUUM DISTILLATION OF HEAVY PRODUCT

CATALYST	TEST NR.	% WEIGHT OF DISTILLATION FRACTIONS (TEMPERATURE IN DEG. C) -250	250-350	350-407	407-450	450-EBP	TOTAL DIST. (% WT.)	END DIST. TEMP. (D C)
HDS-1442-A	17	4.6	10.0	8.1	9.0	15.5	47.2	450
	3		8.3	1.0	2.5	6.0	17.8	460
	14		0.2	0.5	1.0	5.1	6.8	480
	16			1.4	2.2	2.2	5.8	460
	12			NOT DISTILLED				
	15		1.0	0.6	0.9	5.8	8.3	500
	7		1.0	1.3	0.7	8.4	11.4	525
CoMo-CabOsil	23			1.0	1.0	8.0	10.0	520
	18	6.1	1.3	1.7	2.5	27.8	39.4	485
	19	9.1	0.8	0.7	1.6	34.1	46.3	510
	24		0.6	0.9	2.0	13.9	17.4	530
C70-2 (Zn-Cr)	4		9.7	0.2	3.1	6.8	19.8	460
	5		2.5	7.1			9.6	400
	9		1.5	3.8	6.9		12.2	440
Mo(CO)6	10		2.4	1.9	3.1	11.4	18.8	525
FeSO4-CabOsil	11			2.7	8.2		10.9	450
M.A.P.	20				1.0	10.0	11.0	525
H-ZSM-5	21		0.1	0.3		5.9	6.3	525
C70-2/HDS	13			0.3	0.9	7.9	9.1	500
Zn-Cr/M.A.P.	22		0.3	0.7	0.2	11.7	12.9	510
RED MUD	1					100.0	0.0	524
	2			NOT DISTILLED				

TABLE 6

VACUUM RESIDUE ULTIMATE ANALYSIS

CATALYST	TEST NR.	(% WT. ORGANIC RESIDUE BASIS) C (% WT)	H (% WT)	N (% WT)	S (% WT)	ASH (% WT)
HDS-1442-A	17	83.4	6.0	1.2	9.3	25.9
	3	83.3	7.0	1.3	8.4	33.3
	14	85.8	7.0	1.1	6.1	36.8
	16	82.7	7.0	1.0	9.2	31.7
	12	NOT ANALYSED				
	15	85.7	8.0	1.0	6.2	33.6
	7	86.1	6.4	1.4	6.1	26.3
CoMo-CabOsil	23	84.9	8.8	1.1	5.2	19.9
	18	85.7	6.1	1.4	6.8	34.6
	19	86.9	4.6	1.9	7.4	34.9
	24	85.5	7.8	1.4	5.3	28.0
C70-2 (Zn-Cr)	4	87.8	7.3	1.3	3.6	12.1
	5	84.9	7.3	1.1	6.7	6.3
	9	86.3	5.6	1.5	6.6	14.4
Mo(CO)6	10	85.2	7.4	1.4	6.1	9.4
FeSO4-CabOsil	11	85.2	6.1	1.0	7.7	20.7
M.A.P.	20	85.2	7.5	1.2	6.1	8.7
H-ZSM-5	21	84.3	8.9	1.2	5.6	15.1
C70-2/HDS	13	84.7	6.6	1.4	7.2	25.0
Zn-Cr/M.A.P.	22	85.3	7.5	1.0	6.1	12.1
RED MUD	1	NOT ANALYSED				
	2	NOT ANALYSED				

TABLE 7.

COMPOSITION OF LIGHT PRODUCT STREAM

CATALYST	TEST NR.	SEPARATION		AQUEOUS PHASE ANALYSIS		
		OIL PHASE (g)	AQUEOUS PHASE (g)	MEOH (% WT)	H2O (% WT)	OTHERS (% WT)
HDS-1442-A	17	21.3	148.4	35.0%	62.0%	3.0%
	3	60.0	254.0	60.0%	40.0%	0.0%
	14	106.2	176.8	32.0%	66.0%	2.0%
	16	94.9	172.0	45.0%	51.0%	4.0%
	12	73.5	136.8	24.0%	76.0%	1.0%
	15	78.1	194.5	37.0%	52.0%	11.0%
	7	74.0	360.9	41.0%	57.0%	2.0%
CoMo-CabOsil	23	45.2	435.1	80.0%	20.0%	0.0%
	18	52.9	311.3	63.0%	32.0%	5.0%
	19	47.7	349.4	67.0%	31.0%	2.0%
	24	74.0	359.4	68.0%	30.0%	2.0%
C70-2 (Zn-Cr)	4	55.0	380.8	81.0%	16.0%	3.0%
	5	25.0	338.5	84.0%	13.0%	3.0%
	9	47.5	360.7	67.0%	29.0%	4.0%
Mo(CO)6	10	78.2	212.7	71.0%	20.0%	9.0%
FeSO4-CabOsil	11	67.0	135.2	59.0%	39.0%	2.0%
M.A.P.	20	44.0	442.6	77.0%	21.0%	2.0%
H-ZSM-5	21	37.0	397.4	54.0%	46.0%	0.0%
C70-2/HDS	13	84.4	175.0	40.0%	55.0%	5.0%
Zn-Cr/M.A.P.	22	44.1	427.9	83.0%	16.0%	1.0%
RED MUD	1	0.0	194.0	100.0%	0.0%	0.0%
	2	NOT DETERMINED				

TABLE 6

WEIGHT DISTRIBUTION OF LIGHT STREAM

CATALYST	TEST NR.	OIL (g)	MEOH (g)	H2O (g)	OTHER (g)
HDS-1442-A	17	21.3	52.2	92.1	4.1
	3	60.0	152.4	101.6	0.0
	14	106.2	56.5	116.1	4.2
	16	94.9	77.6	87.3	7.1
	12	73.5	32.5	103.5	0.8
	15	78.1	72.4	101.1	21.0
	7	74.0	148.6	204.2	8.1
CoMo-CabOsil	23	45.2	348.6	86.5	0.0
	18	52.9	197.3	98.2	15.8
	19	47.7	235.7	107.1	6.6
	24	74.0	244.4	107.8	7.2
C70-2 (Zn-Cr)	4	55.0	309.0	59.5	12.3
	5	25.0	283.7	43.5	11.3
	9	47.5	242.2	104.0	14.5
Mo(CO)6	10	78.2	150.1	41.6	21.0
FeSO4-CabOsil	11	67.0	79.2	52.1	3.9
M.A.P.	20	44.0	342.5	93.4	6.7
H-ZSM-5	21	37.0	215.9	181.5	.0
C70-2/HDS	13	84.4	70.5	95.6	8.9
Zn-Cr/M.A.P.	22	44.1	355.8	67.2	4.9
RED MUD	1	0.0	194.0	0.0	0.0
	2	NOT DETERMINED			

TABLE 9

SIMULATED DISTILLATION OF OIL PHASE
OF LIGHT PRODUCT

CATALYST	TEST NR.	% WEIGHT OF DISTILLATION FRACTIONS (TEMPERATURE IN DEG. C) -250	250-350	350-407	407-450	450-EBP
HDS-1442-A	17	45.0%	30.0%	12.1%	10.9%	2.0%
	3	32.0%	30.5%	16.6%	13.7%	7.2%
	14	45.0%	27.5%	12.5%	10.0%	5.0%
	16	47.2%	27.3%	13.0%	12.0%	9.0%
	12	50.0%	26.5%	11.5%	7.0%	5.0%
	15	41.0%	29.0%	13.5%	11.5%	5.0%
	7	44.2%	26.6%	13.5%	10.7%	5.0%
CoMo-CabOsil	23	28.0%	25.0%	15.6%	11.3%	20.1%
	18	38.0%	26.1%	15.0%	14.1%	6.8%
	19	35.0%	26.1%	14.2%	9.8%	14.9%
	24	40.1%	26.2%	13.4%	8.3%	12.0%
C70-2 (Zn-Cr)	4	42.0%	29.0%	15.0%	9.0%	5.0%
	5	75.5%	15.5%	4.0%	3.5%	1.5%
	9	70.0%	20.6%	4.4%	2.5%	2.5%
Mo(CO)6	10	43.5%	30.5%	11.0%	10.0%	5.0%
FeSO4-CabOsil	11	54.0%	31.0%	9.0%	3.0%	3.0%
M.A.P.	20	24.9%	26.5%	16.4%	12.5%	19.7%
H-ZSM-5	21	32.8%	24.0%	14.5%	10.7%	18.0%
C70-2/HDS	13	41.8%	28.2%	14.0%	11.0%	5.0%
Zn-Cr/M.A.P.	22	32.5%	27.9%	14.7%	9.4%	15.5%
RED MUD	1	NOT DETERMINED				
	2	NOT DETERMINED				

TABLE 10

GAS ANALYSIS - TESTS USING THE HDS-1442-A CATALYST

TEST NUMBER	TIME OF COLLECTION (MIN)	PERCENT VOLUME OF GAS SAMPLE							GAS VOLUME (STP 1)
		H2	CO2	C2H6	H2S	CH4	CO	DME+C3	
17	5	14	18	0	0	28	0	37	9.2
	20	8	20	0	0	48	0	24	17.9
	70	0	23	0	0	63	0	14	16.4
	120	1	25	0	0	66	0	6	150.6
3	4	19	16	0	0	28	0	37	50.0
	38	6	16	0	0	40	0	38	30.0
	83	1	20	0	0	54	0	25	13.0
	125	1	27	1	0	74	0	2	146.9
14	5	12	8	1	0	25	2	53	10.6
	30	12	12	1	0	39	1	34	13
	60	11	15	2	0	48	1	24	16.3
	90	9	17	2	0	56	1	15	12.2
	120	8	18	3	0	63	1	8	122.5
16	1	11	21	0	0	52	0	17	38
	33	1	24	1	1	71	0	4	39.2
	93	1	23	1	2	69	0	5	6
	120	1	23	1	2	70	0	3	131.3
12	45	12	14	3	0	56	2	15	7.6
	120	2	17	4	1	70	0	6	126.5
15	5	10	8	1	0	23	2	57	9
	30	11	12	1	0	37	2	38	13.8
	60	13	16	2	0	55	1	14	129.3
7	35	7	7	1	0	17	1	68	10
	90	7	9	1	0	26	1	56	10.5
	120	12	16	3	0	57	1	11	80.2

TABLE 11

GAS ANALYSIS - TESTS USING THE CoMo-CatOSil CATALYST

TEST NUMBER	TIME OF COLLECTION (MIN)	PERCENT VOLUME OF GAS SAMPLE							GAS VOLUME (STP l)
		H2	CO2	C2H6	H2S	CH4	CO	DME+C3	
23	0	26	12	0	0	36	3	23	13.0
	17	26	17	0	0	34	3	21	15.5
	60	23	18	0	0	42	2	14	122.6
18	0	23	14	0	0	26	2	33	14.9
	15	19	16	0	0	33	0	30	15.9
	90	6	18	0	0	44	0	31	9.2
	120	6	20	1	0	61	0	13	141.4
19	2	24	12	0	0	36	3	25	6.4
	6	25	16	0	0	36	3	22	12.4
	39	21	18	0	0	38	2	22	18.5
	120	14	20	1	0	49	1	14	128.1
24	1	17	10	0	0	38	3	31	11.3
	164	10	20	1	0	48	1	20	53.3
	240	5	21	1	0	57	1	15	125.1

TABLE 12

GAS ANALYSIS - TESTS USING THE C-70-2 CATALYST

TEST NUMBER	TIME OF COLLECTION (MIN)	PERCENT VOLUME OF GAS SAMPLE							GAS VOLUME (STP l)
		H2	CO2	C2H6	H2S	CH4	CO	DME+C3	
4	11	41	19	0	0	17	3	21	32.8
	41	27	26	0	0	16	2	30	23.8
	127	30	18	1	0	42	2	8	16.9
	144	28	19	1	0	41	2	11	135.1
5	175	47	18	1	0	25	4	5	202.4
9	4	62	21	0	0	7	0	10	2.5
	42	58	20	0	0	12	1	9	29.5
	81	58	18	1	0	13	2	8	25.6
	196	57	20	1	0	16	3	4	106.9

TABLE 13

CHROMATOGRAPHIC ANALYSIS OF GAS SAMPLES OF TEST NOS 10, 11, 20, 21, 13, 22, 2

TEST NUMBER	TIME OF COLLECTION (MIN)	PERCENT VOLUME OF GAS SAMPLE							GAS VOLUME (STP l)
		H2	CO2	C2H6	H2S	CH4	CO	DME+CO	
10	0	28	10	0	0	26	28	18	6.1
Mo(CO)6	46	17	14	0	0	29	7	34	42.3
	120	4	25	1	0	61	1	9	128.9
11	120	6	18	2	0	63	0	1	112.2
FeSO4-CAB									
20	7	9	11	1	0	30	1	49	2.5
M.A.P.	70	10	11	1	0	43	2	33	17.2
	120	26	10	1	0	46	2	12	62.1
21	5	1	1	0	0	2	0	96	7.9
H-ZSM-5	60	3	2	0	0	8	0	87	5.3
	120	10	8	1	0	34	1	45	72.5
13	5	29	12	0	0	14	1	45	17.4
C702+MOS	33	25	15	1	0	25	1	34	17.9
	66	19	16	1	0	33	1	31	13.6
	95	15	18	1	0	43	1	22	8.9
	120	14	20	1	0	54	1	10	134.8
22	0	51	16	0	0	11	2	20	4.1
C702+MAP	8	51	17	0	0	16	3	17	8.1
	30	50	17	0	0	16	2	15	12.1
	90	47	17	0	0	18	2	15	23.0
	120	53	17	0	0	21	2	6	138.8
2	120	7.2	6.5	2.1	0	78.4	3	2.2	46.0
RED MUD									

TABLE :4

ELEMENTAL ANALYSIS OF THE DISTILLATE
PRODUCT OF TEST Nos 3, 10, 18

TEST	CATALYST	C (% WT)	H (% WT)	N (% WT)	S (% WT)
3	HDS-1442A	82.4	10.9	0.8	3.0
10	Mo(CO)$_6$	81.1	11.5	0.3	3.1
18	CoMo-Cat.C-411	81.2	11.5	0.6	3.5

TABLE 15

PROPERTIES OF ATHABASCA PITCH (524°C)

SOLVENT EXTRACTION	% Wt.
Oils (heptane solubles)	73.4
Asphaltenes (Tol Sol - hept sol.)	25.1
Preasphaltenes (THF sol - Tol sol.)	0.0
Solids (THF Insolubles)	1.5
ELEMENTAL ANALYSIS	
Carbon	82.1
Hydrogen	9.0
Nitrogen	0.9
Sulphur	5.7
Oxygen (by difference)	2.3

TABLE 16

TEST NR.	CATALYST	ACTIVE AGENT	SUPPORT	SUPPLYER
2	RED MUD	Fe_2O_3	none	obtained as a by-product in Al extraction
3,7,12,14 15,16 &17	AERO HDS 1442A	CoO,MoO_3	Alumina	AMERICAN CYANAMID
4 & 9	C 70-2	InO,Cr_2O	none	UNITED CATALYSTS
10	Molybdenum Hexacarbonyl	Mo	none	ALDRICH CHEMICALS
21	H-ISM 5		zeolite	CANMET 1)
20	M.A.P.		carbonaceous	CANMET 1)
18 &19	CoMo-Cab O Sil	CoO,MoO_3	silica	in-house prepared
11	$FeSO_4$-Cab O Sil	FeS	silica	in-house prepared

TABLE 17.

PITCH CONVERSION AND
DISTILLATE YIELD
(% WT. PITCH FEED)

CATALYST	TEST NR.	PITCH CONVER.	DIST. YIELD	MEOH CONSUM.
HDS-1442-A	17	59.0	56.5	110.0
	3	61.1	54.5	263.0
	14	45.9	43.8	122.0
	16	45.7	3c.8	107.0
	12	46.5	27.8	82.0
	15	38.0	38.2	124.0
	7	46.2	43.1	114.0
CoMo-CabOsil	23	36.4	31.3	123.0
	18	63.5	62.7	177.0
	19	68.4	64.8	146.0
	24	53.7	46.7	157.0
C70-2 (Zn-Cr)	4	42.7	42.9	146.0
	5	21.0	21.3	108.0
	9	38.6	30.1	68.0
Mo(CO)6	10	47.8	47.1	108.0
FeSO4-CabOsil	11	39.4	37.9	83.0
M.A.P.	20	32.6	29.5	89.0
H-ZSM-5	21	26.8	23.7	162.0
C70-2/HDS	13	44.6	45.6	150.0
Zn-Cr/M.A.P.	22	32.0	32.3	107.0
RED MUD	1	NOT DETERMINED		1
	2	NOT DETERMINED		2

TABLE.3

PRODUCT DISTRIBUTION
(% WT PITCH FEED)

CATALYST	TEST NR.	ATMOS. DIST.	VACUUM DIST.	NON. DIST.	SOLIDS THF
HDS-1442-A	17	21.4	36.4	34.8	6.2
	3	31.6	22.9	33.6	5.3
	14	27.4	16.3	36.9	17.3
	16	20.7	13.1	40.7	13.6
	12	21.3	6.6	8.9	45.4
	15	24.3	17.7	46.6	15.4
	7	22.7	17.7	39.2	14.6
CoMo-CabOsil	23	11.8	19.5	63.4	0.2
	18	24.4	36.7	32.2	4.3
	19	22.6	42.2	28.6	2.8
	24	22.5	24.2	42.7	3.6
C70-2 (Zn-Cr)	4	26.8	16	52.7	4.6
	5	13.3	7.9	53.8	25.2
	9	11.6	9.5	10.3	19.9
Mo(CO)6	10	26.6	20.5	50.3	1.9
FeSO4-CabOsil	11	23.6	14.8	42.2	18.4
M.A.P.	20	9.6	19.9	42.9	24.6
H-ZSM-5	21	10.3	13.4	74.6	0
C70-2/HDS	13	27.4	19	41.5	13.9
Zn-Cr/M.A.P.	22	12	20.3	55.9	12.1
RED MUD	1			NOT DETERMINED	
	2			NOT DETERMINED	

ATMO. DIST. : - 350 deg c
VACUUM DIST. : 350 - EDP Deg. C
NON-DIST : Residue soluble in THF
SOLIDS : Residue inscluble in THF

MeOH FROM NAT GAS, BASE CASE

TABLE 19.

FINANCIAL MODEL (BEFORE TAX) PITCH UPGRADING BY TREATMENT WITH MeOH

PROJECTED EARNINGS

YEARS	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
PRODUCT REVENUES (MILLION U.S.$)	99.5	104.5	109.7	115.2	120.9	127.0	133.3	140.0	147.0	154.4	162.1	170.2	178.7	187.6	197.0	206.8	217.2	228.0	239.5	251.4
EXPENSES																				
CAPITAL CHARGES	10.6	10.6	10.6	10.6	10.6	10.6	10.6	10.6	10.6	10.6	10.6	10.6	10.6	10.6	10.6	10.6	10.6	10.6	10.6	10.6
BITUMEN	27.1	28.5	29.9	31.4	33.0	34.6	36.3	38.1	40.1	42.1	44.2	46.4	48.7	51.1	53.7	56.4	59.2	62.1	65.2	68.5
OTHER (NAT. GAS)	24.7	25.9	27.2	28.6	30.0	31.5	33.1	34.7	36.5	38.3	40.2	42.2	44.3	46.6	48.9	51.3	53.9	56.6	59.4	62.4
METHANOL	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
POWER	3.9	4.1	4.2	4.4	4.6	4.7	4.9	5.1	5.3	5.5	5.8	6.0	6.2	6.5	6.7	7.0	7.3	7.6	7.9	8.2
O&M	9.3	9.6	10.0	10.4	10.8	11.3	11.7	12.2	12.7	13.2	13.7	14.2	14.8	15.4	16.0	16.7	17.3	18.0	18.7	19.5
IN PLANT FUEL	5.2	5.5	5.7	5.9	6.2	6.4	6.7	6.9	7.2	7.5	7.8	8.1	8.5	8.8	9.1	9.5	9.9	10.3	10.7	11.1
CHEM.&CATALYSTS	9.3	9.7	10.2	10.7	11.2	11.8	12.4	13.0	13.7	14.4	15.1	15.9	16.6	17.5	18.3	19.2	20.2	21.2	22.3	23.4
RESIDUALS(CREDIT)	-5.6	-5.8	-6.0	-6.3	-6.5	-6.8	-7.1	-7.3	-7.6	-7.9	-8.2	-8.6	-8.9	-9.3	-9.6	-10.0	-10.4	-10.9	-11.3	-11.7
BY-PRODUCT (CREDIT)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TOTAL EXPENSES	84.5	88.0	91.8	95.7	99.8	104.1	108.7	113.4	118.4	123.6	129.1	134.8	140.8	147.1	153.7	160.6	167.9	175.5	183.5	191.9
NET EARNINGS	15.0	16.4	17.9	19.5	21.1	22.9	24.7	26.6	28.6	30.8	33.0	35.4	37.9	40.5	43.3	45.2	49.3	52.5	55.9	59.5
EQUITY	135.0																			
NET CASH	-120.0	16.4	17.9	19.5	21.1	22.9	24.7	26.6	28.6	30.8	33.0	35.4	37.9	40.5	43.3	46.2	49.3	52.5	55.9	59.5

CAPITAL COST/DAILY BBL	$18,756
INTERNAL RATE OF RETURN	19.7%
NET P V 8%	152.8

Sandwell Technologies

TABLE 20.

MeOH FROM NAT GAS, BASE CASE

SUMMARY OF ASSUMPTIONS USED IN MODEL

TECHNICAL ASSUMPTIONS		PRICING ASSUMPTIONS		INFLATION ASSUMPTIONS		FINANCING ASSUMPTIONS	
C4+ PRODUCTION(BBLS/SD)	10000	CRUDE OIL BENCHMARK($US/BBL)	$27.50	OVERALL RATE(%/ANNUM)	4.00%	TOTAL INVESTMENT (MILLION US $'S)	$225.1
PITCH USE(MF TPD)							
PROCESS	1450	DISTILLATE PRODUCT	$32.91	RELATIVE RATES		DEBT FINANCING(% OF TOTAL)	40.00%
STEAM	218	NON-DIST. PRODUCT	$19.25	PRODUCTS	1.00%		
TOTAL	1668			GAS	0.00%	INTEREST RATE(%/ANNUM)	10.00%
METHANOL/PITCH RATIO	1.5	PITCH ($/TONNE)	$48.40	PITCH	0.00%		
METHANOL USE(TPD)	870			O&M	0.00%	AMORTIZATION PERIOD(YRS)	20.00
METHANOL RECYCLE	0.90	NATURAL GAS($US/1000 SCF)	$3.00	POWER	0.00%		
TOTAL FEED TO UPGRADER	3626	METHANOL ($/TONNE)	$139.43	RESIDUALS	0.00%	ANNUAL CAPITAL CHARGE(%)	11.75%
HYDROTREATER FEED	989	PURCHASED POWER($US/KWH)	$0.04				
DISTIL.YIELD(BBLS/MAF T)	5.14					EQUITY INVESTMENT (MILLION US $'S)	$135.0
C4+ YIELD (BBLS/MAF T)	6.89						
		RESIDUALS($US/M BTU)	$1.25				
PITCH CONVERSION(% FEED)	68.00%						
OPERATING FACTOR	92.00%	BITUMEN($US/BBL)	$22.50				
NAPHT HYDRTR(YES=1,NO=0)	1						
LGO HYDROTR(YES=1,NO=0)	1						
HGO HYDROTR(YES=1,NO=0)	1						
INPLANT FUEL(NAT GAS=1,C1C2=0)	1						
POWER USE(KWH/T)	200						

TABLE 21.

CAPITAL COST SUMMARY TABLE

AREA/ITEM	UNITS	COST BASIS	FACTOR	THROUGHPUT BASIS	TOTAL AREA COST ($s)
UPGRADER	1	FEED(TPD PITCH)	$18,000	1450	$26,107,388
GAS RECOVERY	1	THRUPUT(TPD PITCH)	$6,700	3170	$21,242,030
DISTILLATION	1	THRUPUT DISTILLATE (BPD)	$420	7462	$3,133,907
METHANOL BY PARTIAL OXIDATION	0	METHANOL (TPD)	$76,000	0	$0
METHANOL FROM NAT. GAS	1	METHANOL (TPD)	$66,500	870	$57,871,377
HYDROTREATERS	1	DIST. THRUPUT (TPD)	$18,000	989	$17,805,239
PURCHASE METHANOL	0	METHANOL USE (TPD)	$0		$0
MISCELLANEOUS	1	TOTAL PLANT FEED(MF TPD)	$12,100	2321	$28,079,946
SUB-TOTAL					$154,239,887
CONTINGENCY			20.00%		$30,847,977
ENGINEERING & DESIGN			8.00%		$2,467,836
SUB-TOTAL					$187,555,703
WORKING CAPITAL,START-UP,FDC,ETC			20.00%		$37,511,141
TOTAL CAPITAL INVESTMENT					$225,066,844

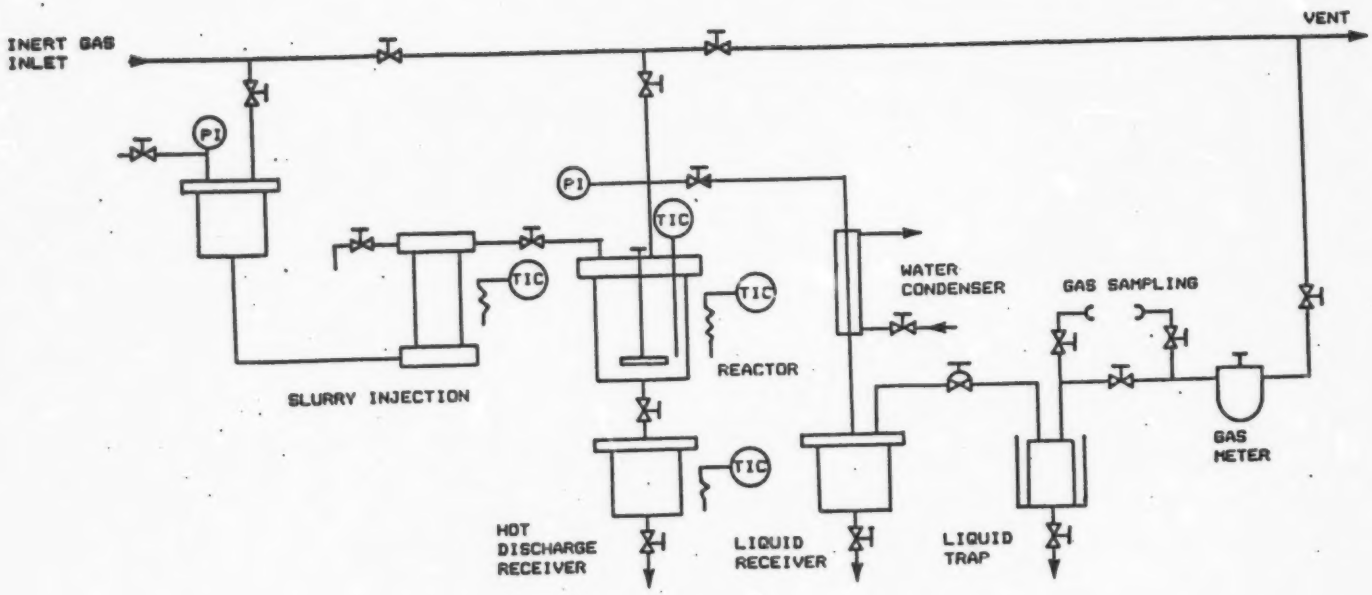


FIGURE 1 SCHEMATIC DIAGRAM OF HOT CHARGE/DISCHARGE REACTOR SYSTEM

Figure 2.

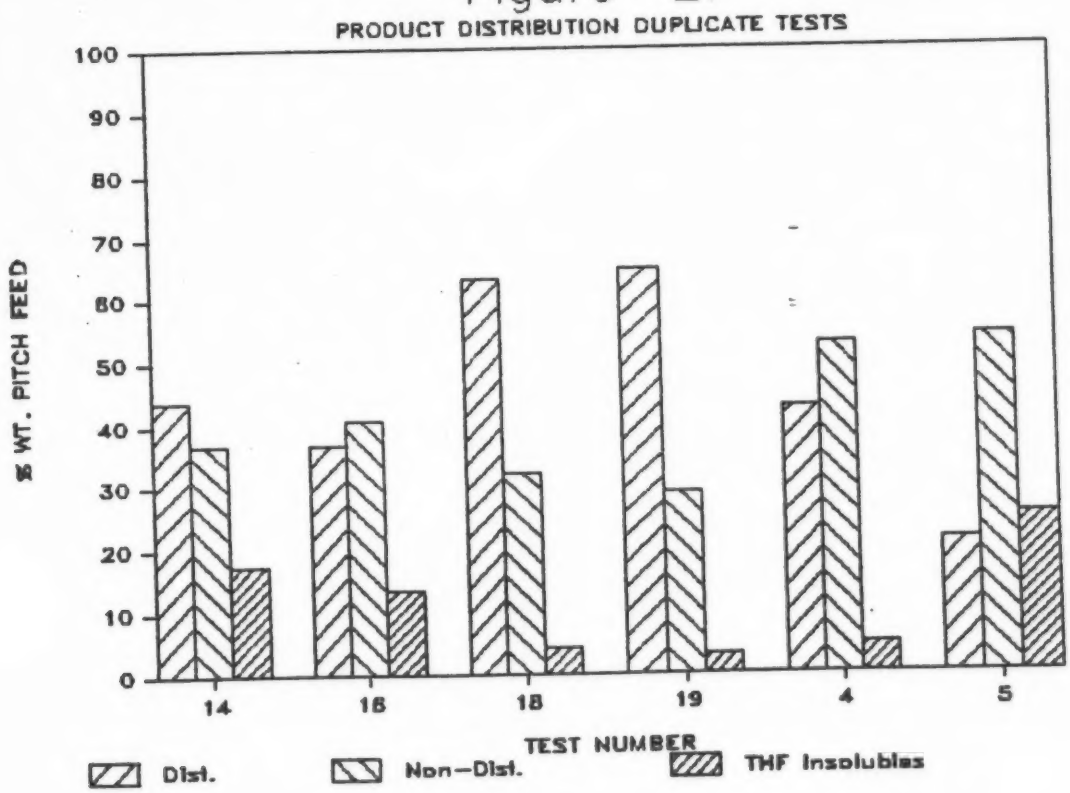

PRODUCT DISTRIBUTION DUPLICATE TESTS
% WT. PITCH FEED
100
90
80
70
60
50
40
30
20
10
0
14
16
18
19
4
5
TEST NUMBER
Dist.
Non-Dist.
THF Insolubles

Figure 3.

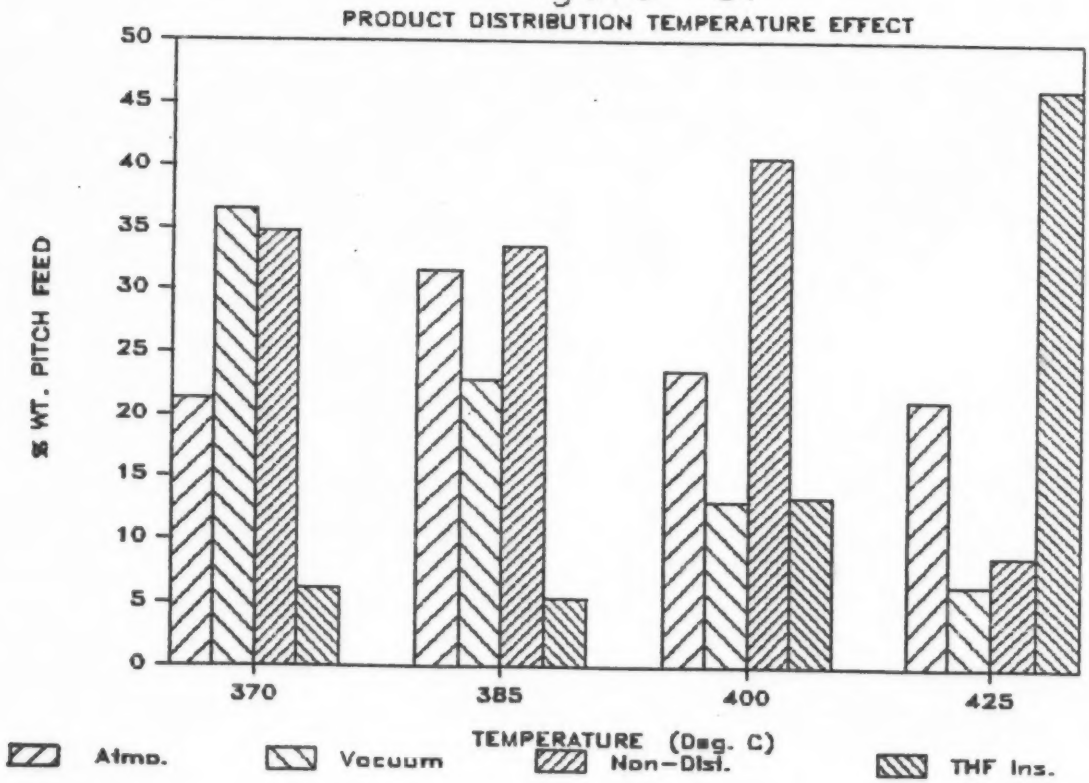

PRODUCT DISTRIBUTION TEMPERATURE EFFECT
% WT. PITCH FEED
50
45
40
35
30
25
20
15
10
5
0
370
385
400
425
TEMPERATURE (Deg. C)
Atmo.
Vacuum
Non-Dist.
THF Ins.

Figure 4.

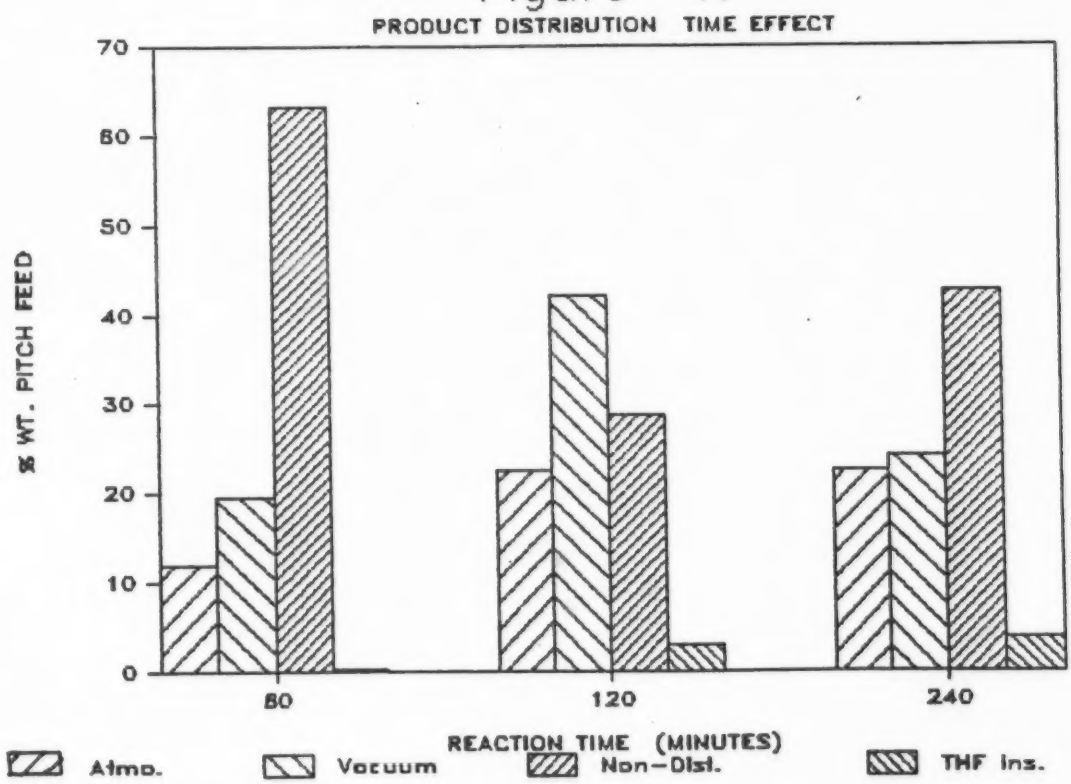

PRODUCT DISTRIBUTION TIME EFFECT
% WT. PITCH FEED
70
60
50
40
30
20
10
0
80
120
240
REACTION TIME (MINUTES)
Atmo.
Vacuum
Non-Dist.
THF Ins.

Figure 5.

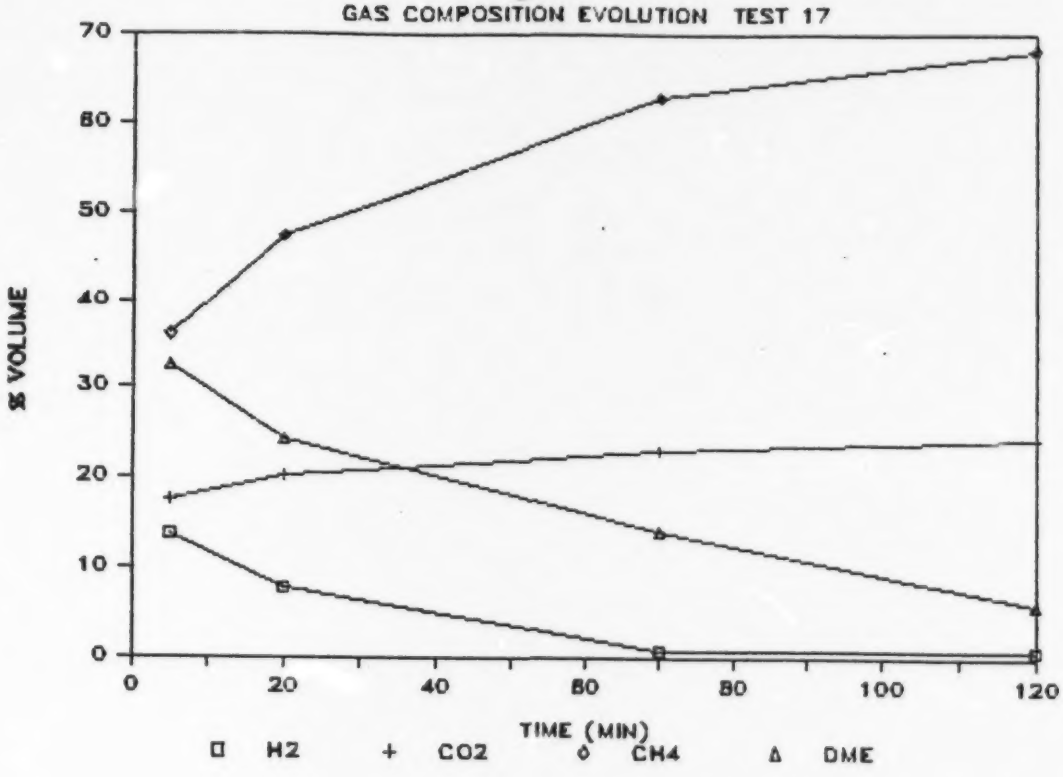


Figure 6.

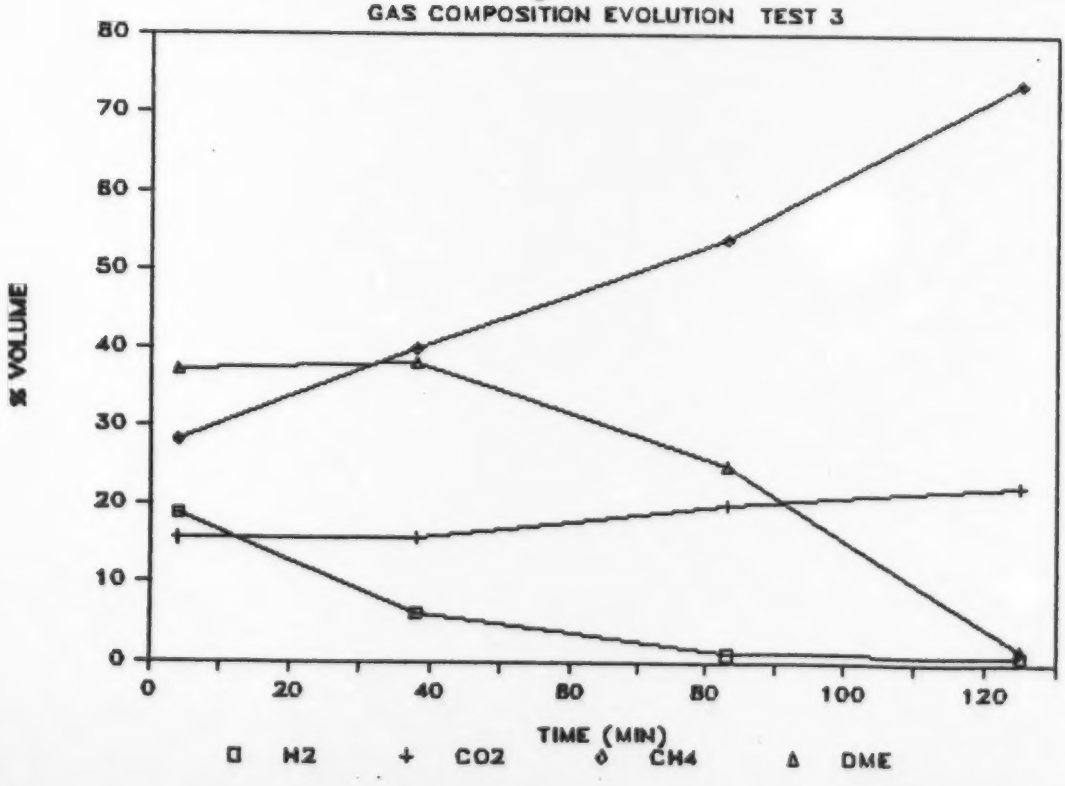


Figure 7.

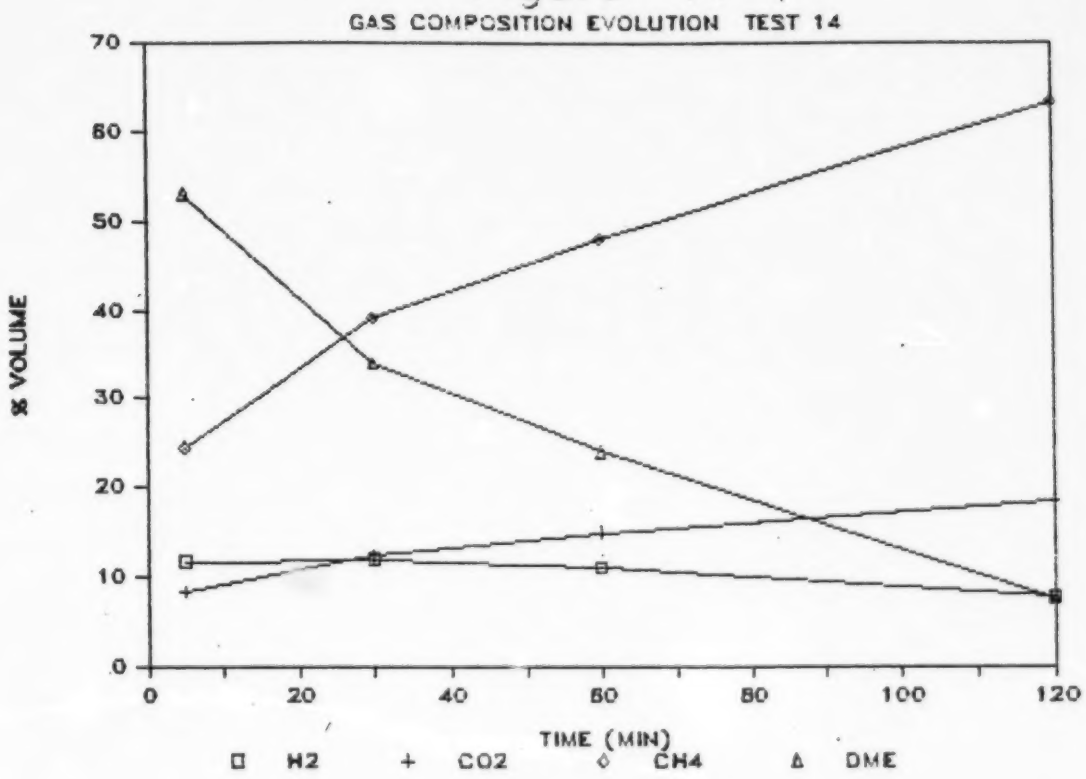


Figure 8.

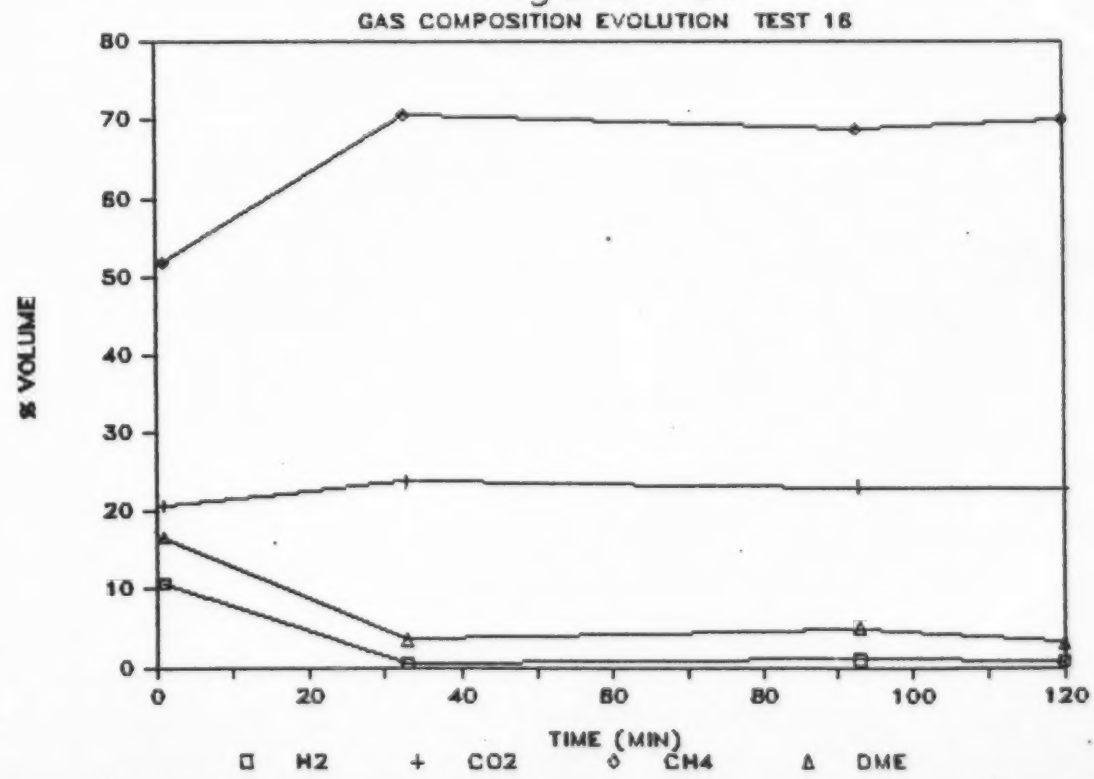


Figure 9.

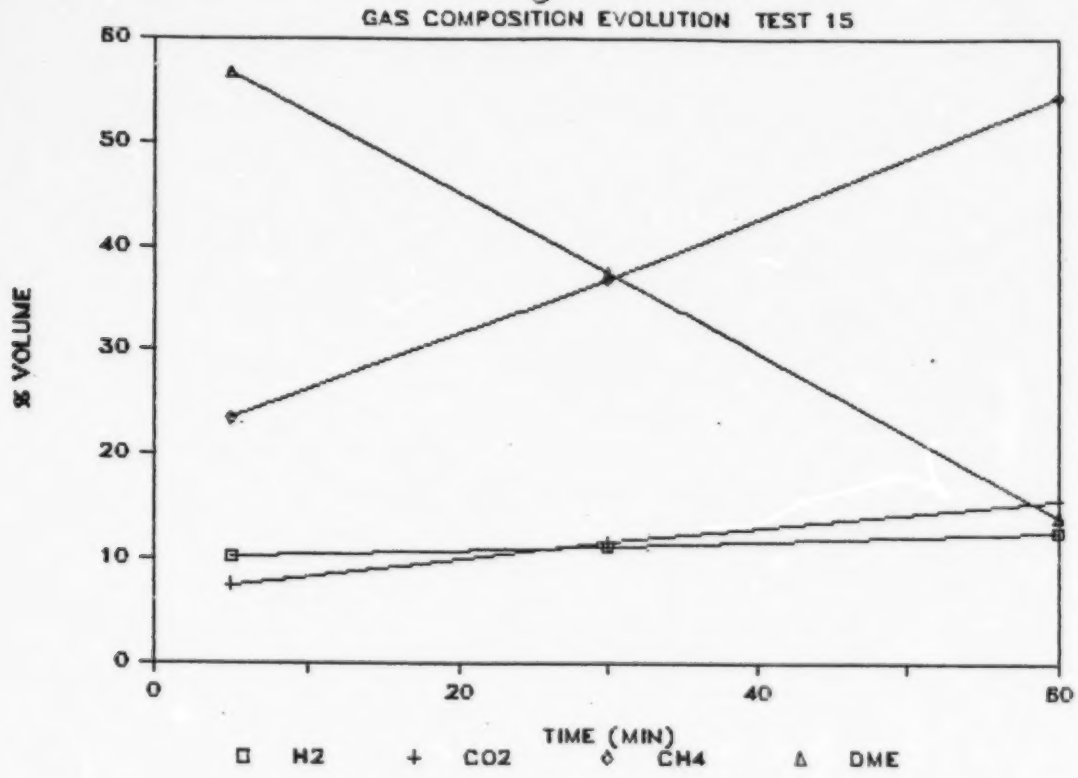


Figure 10.

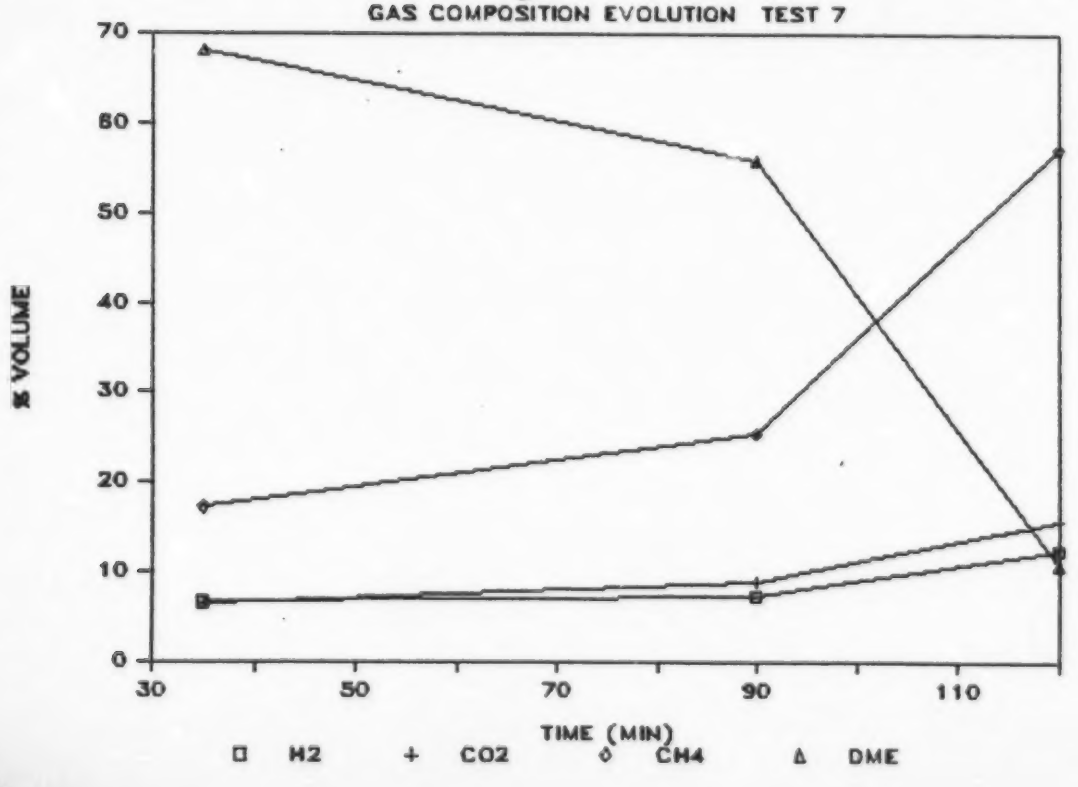


FIGURE 11.

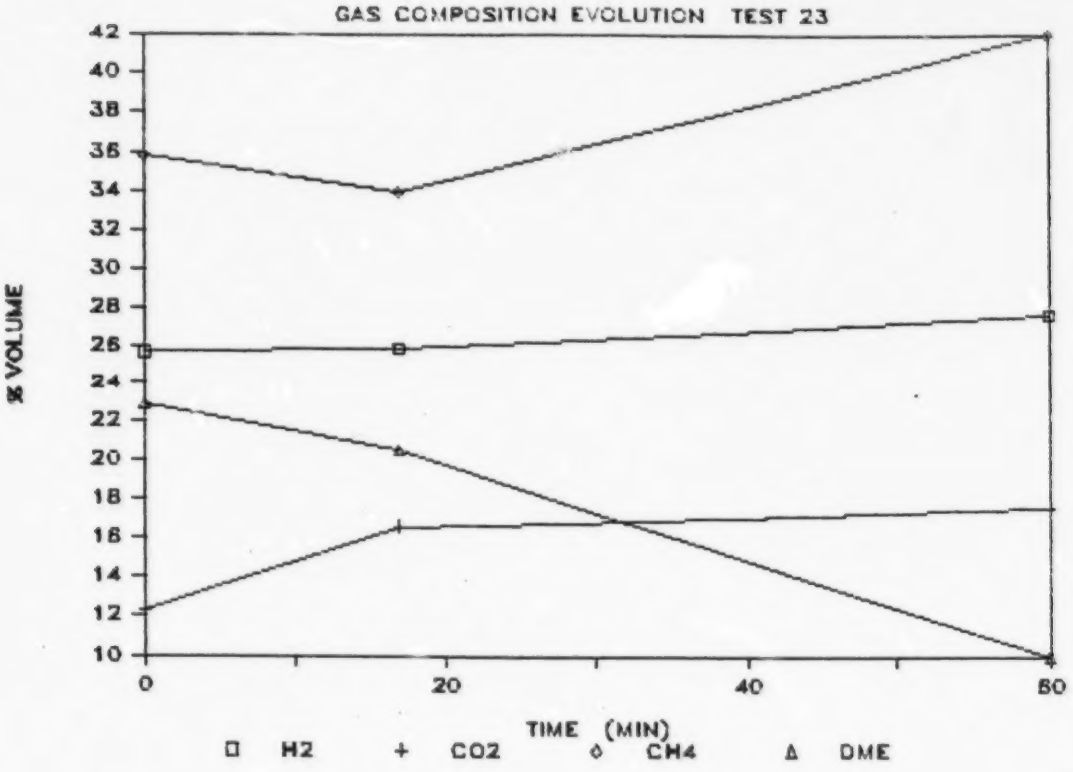


FIGURE 12.

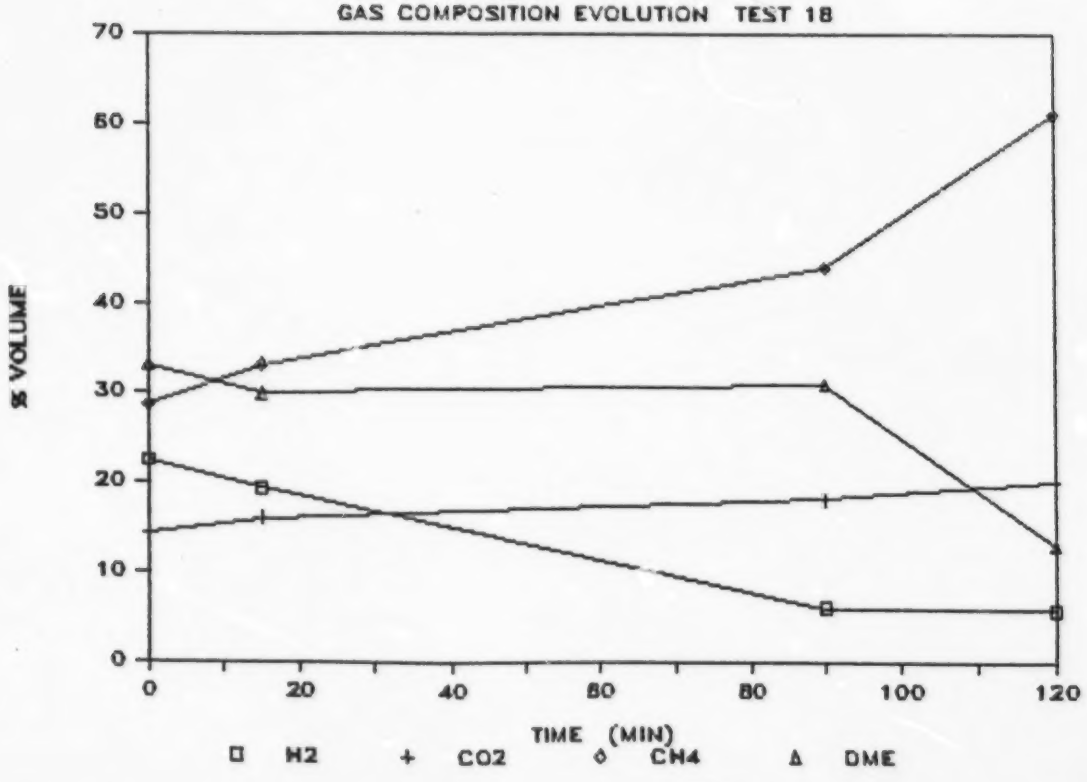


Figure 13.

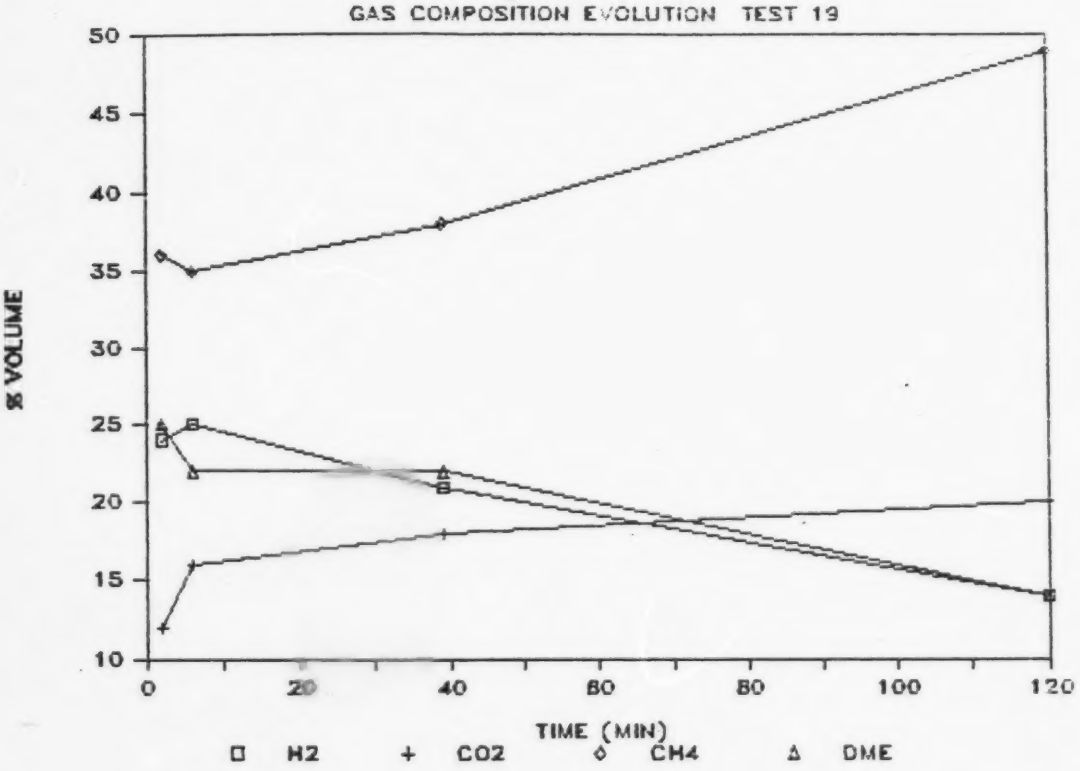


Figure 14.

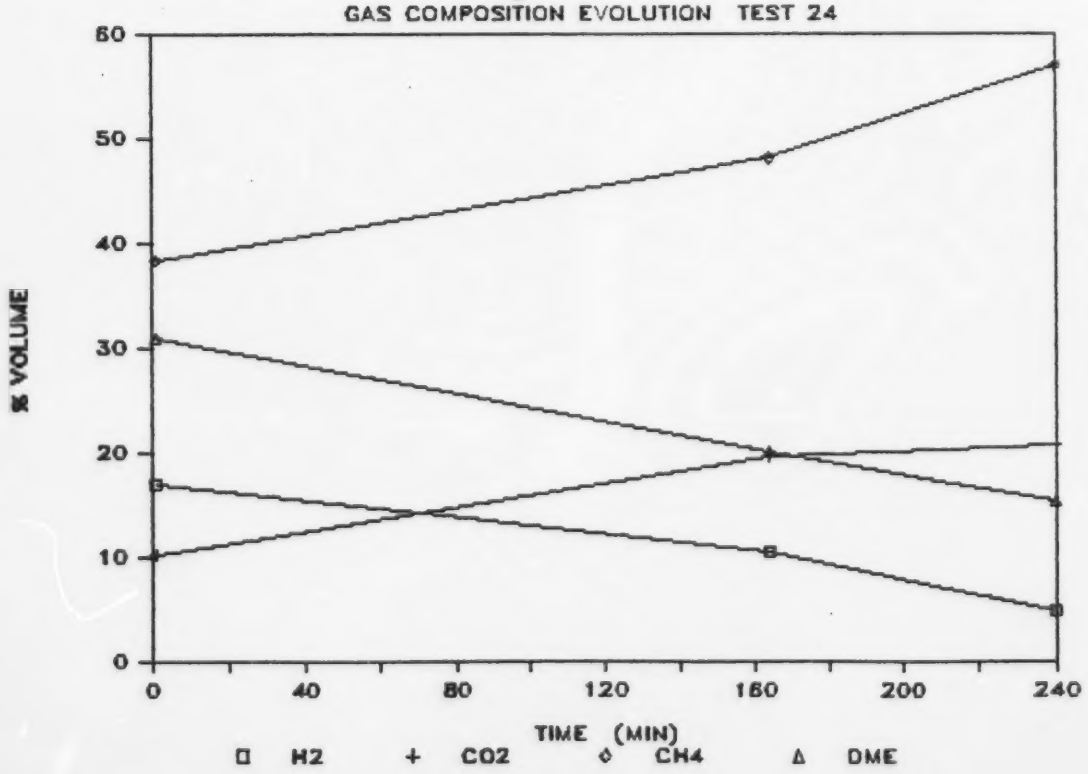


Figure 15.

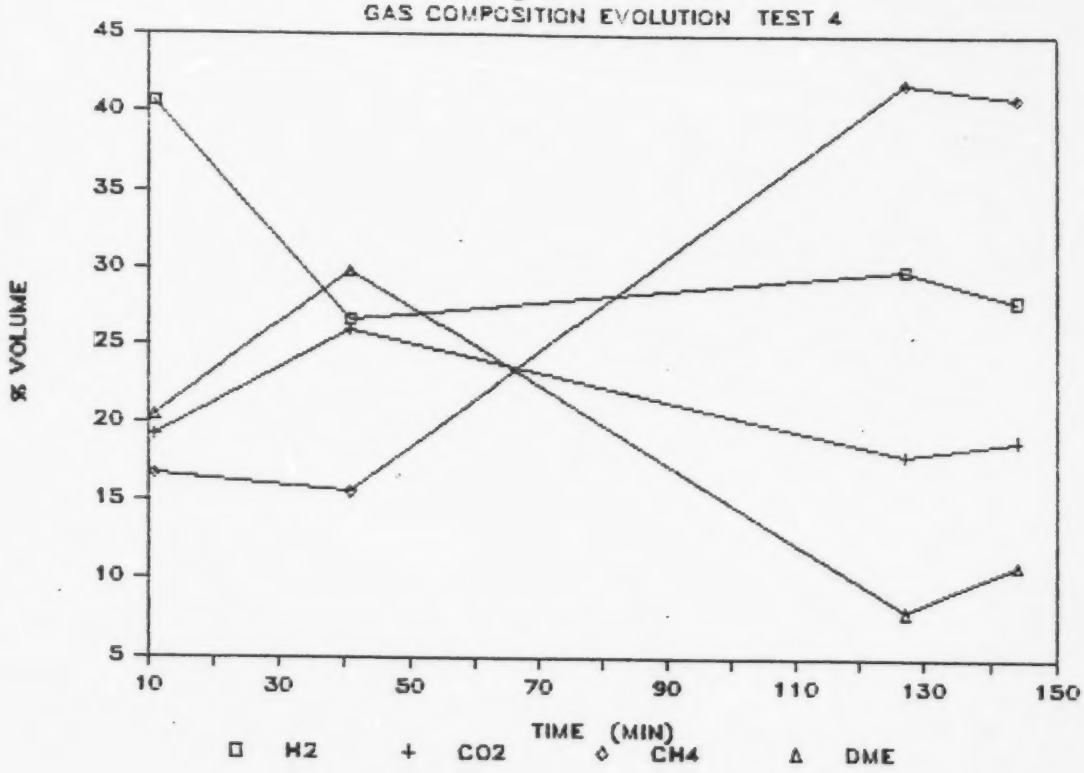


Figure 16.

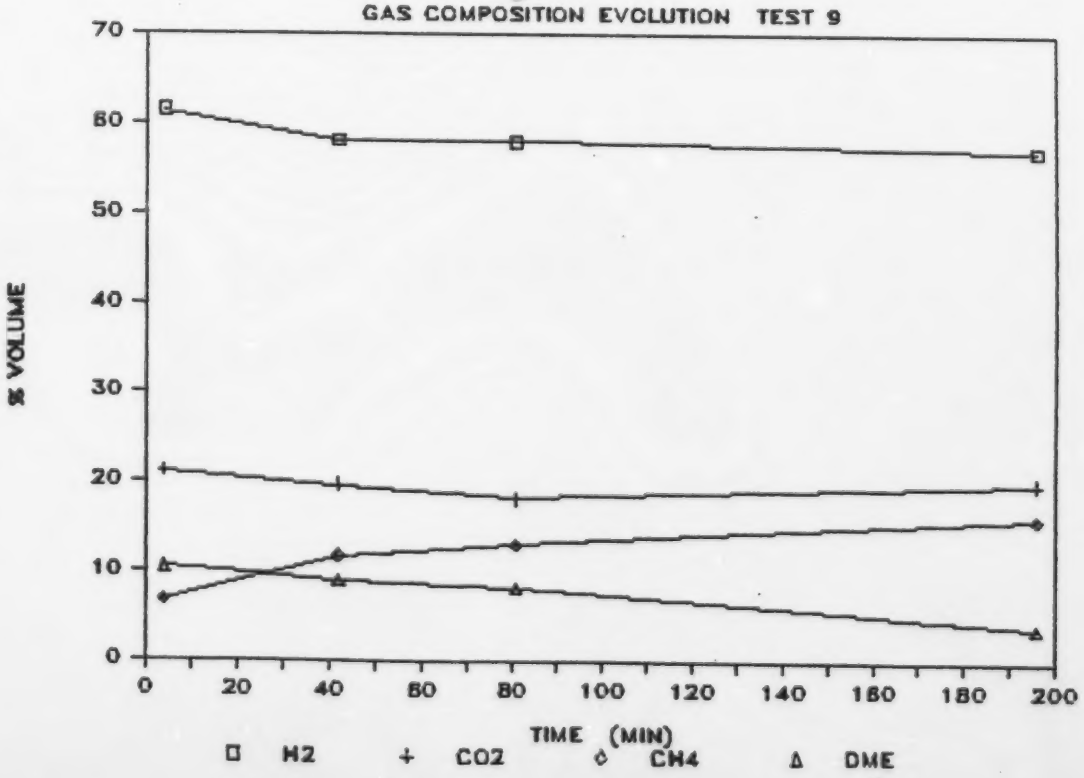


Figure 17.

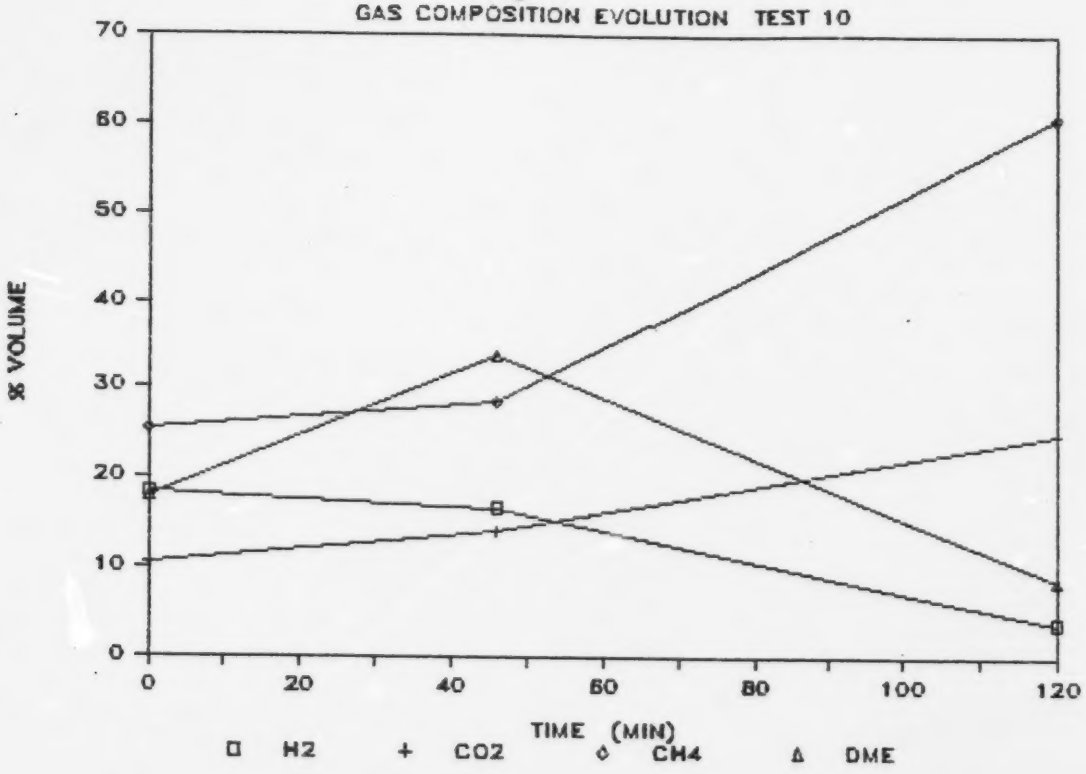


Figure 18.

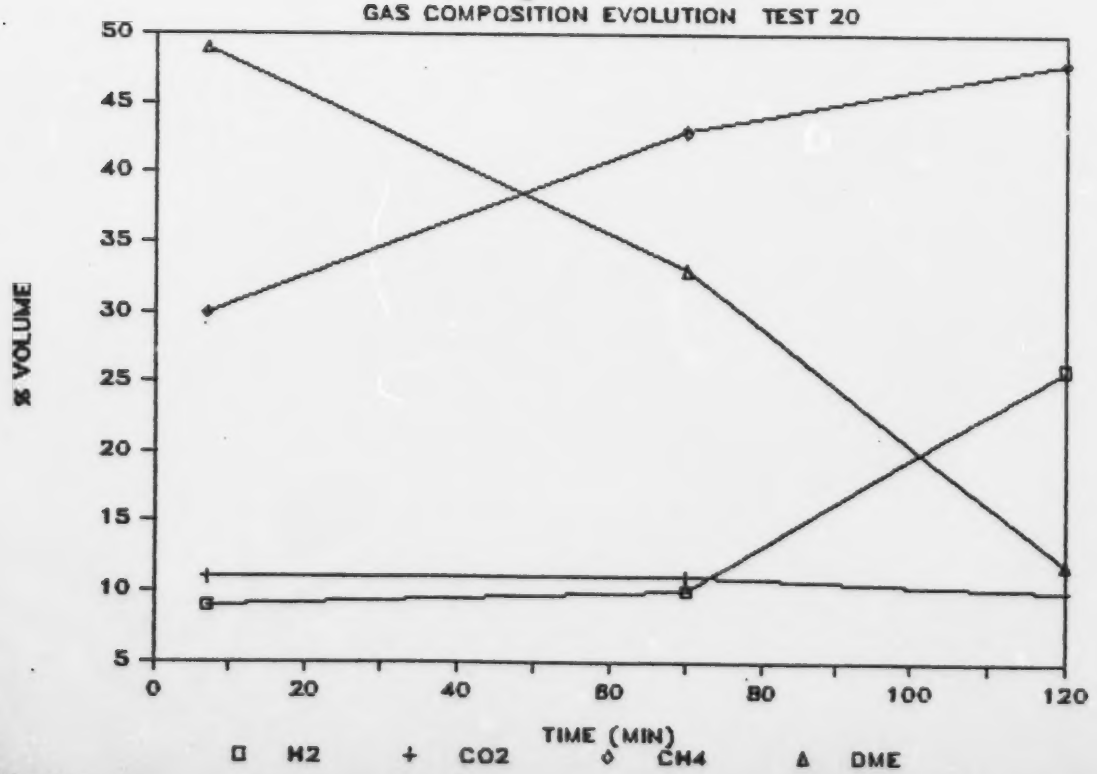


Figure 19.

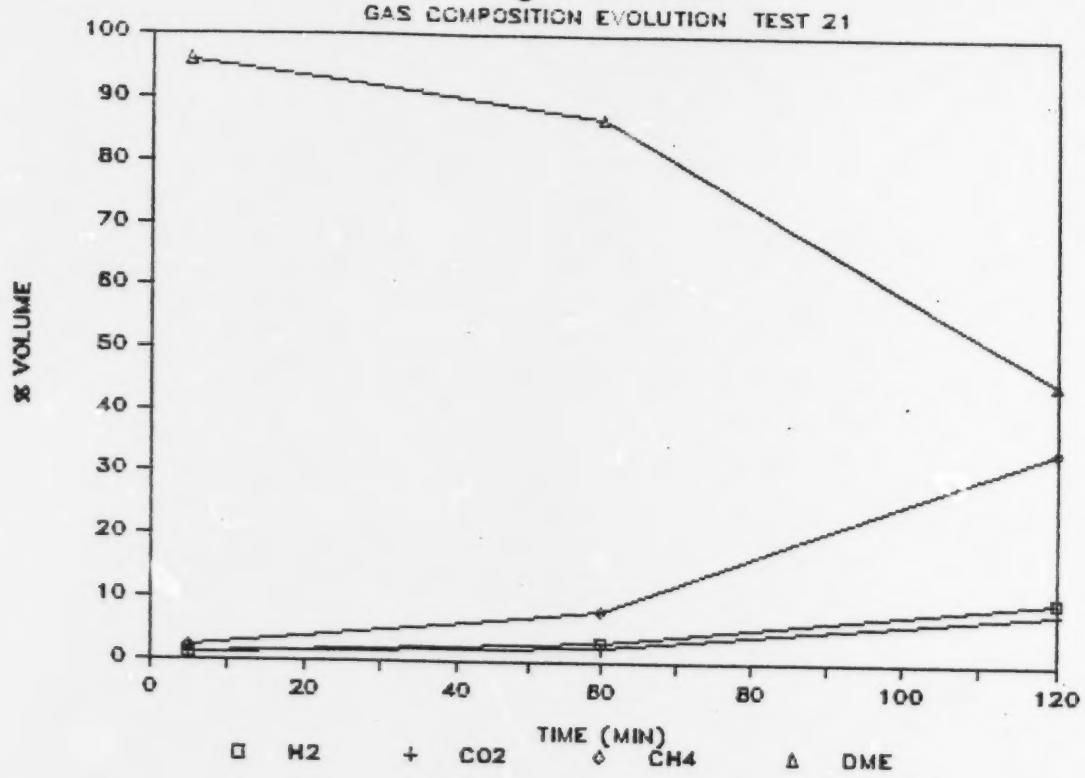


Figure 20.

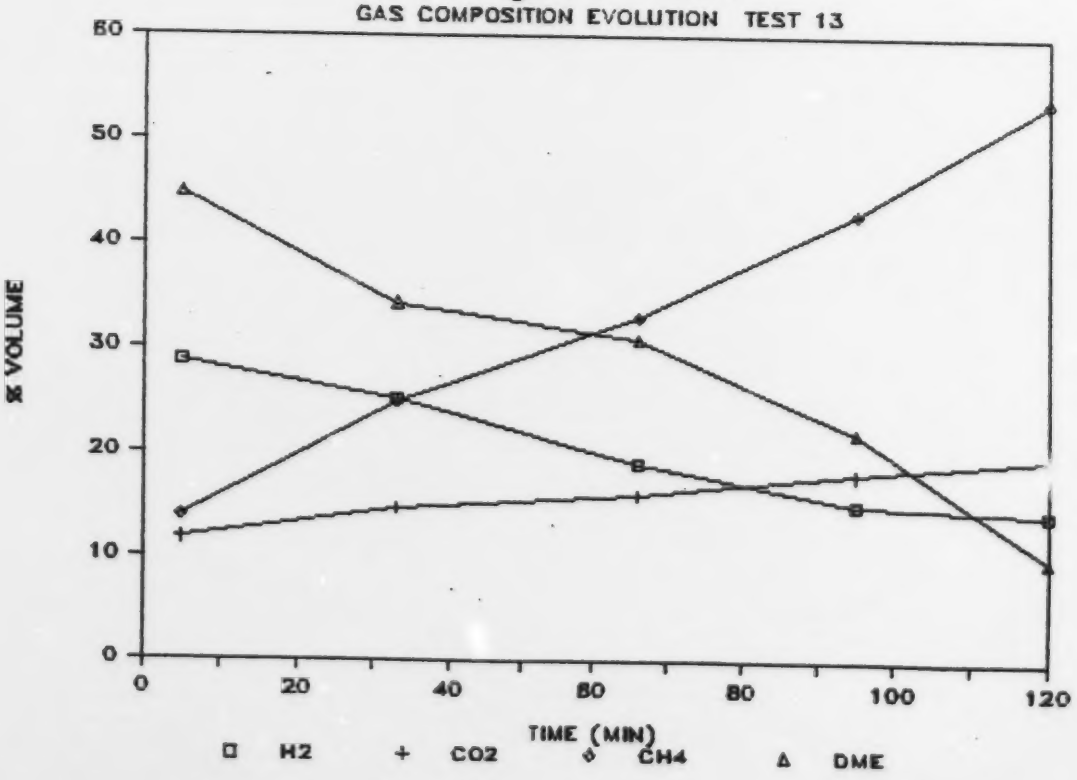


Figure 21.

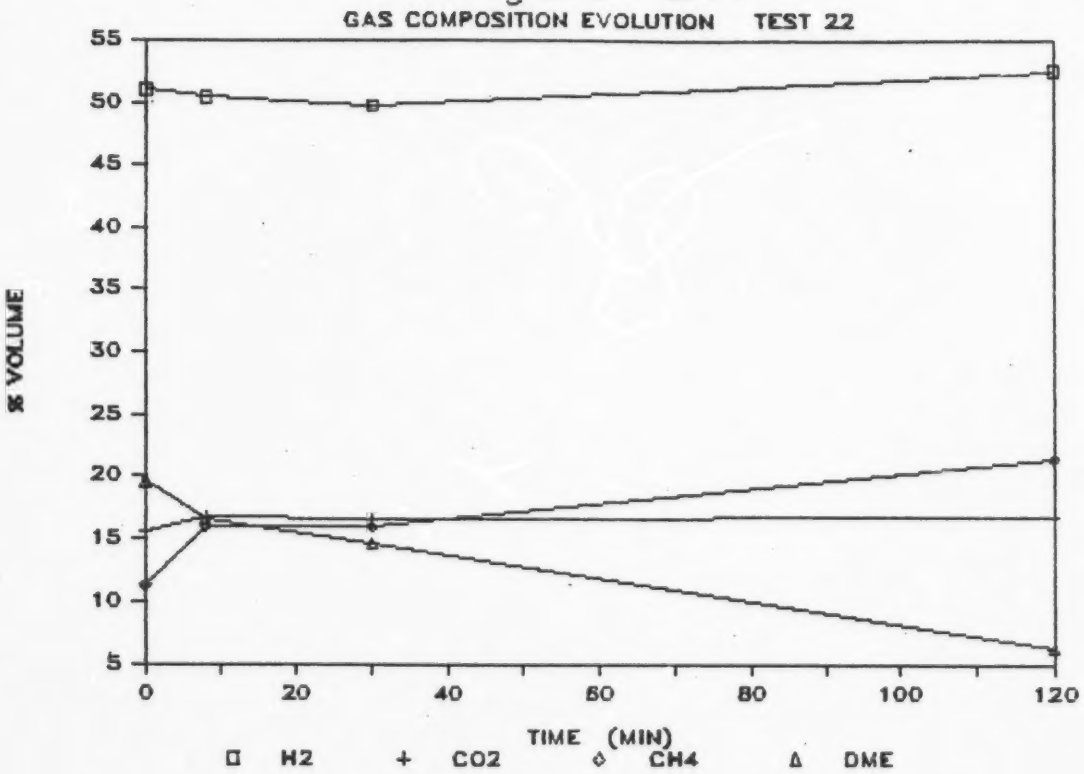

GAS COMPOSITION EVOLUTION TEST 22
% VOLUME
55
50
45
40
35
30
25
20
15
10
5
0
20
40
60
80
100
120
TIME (MIN)
□ H2
+ CO2
◇ CH4
Δ DME

Figure 22

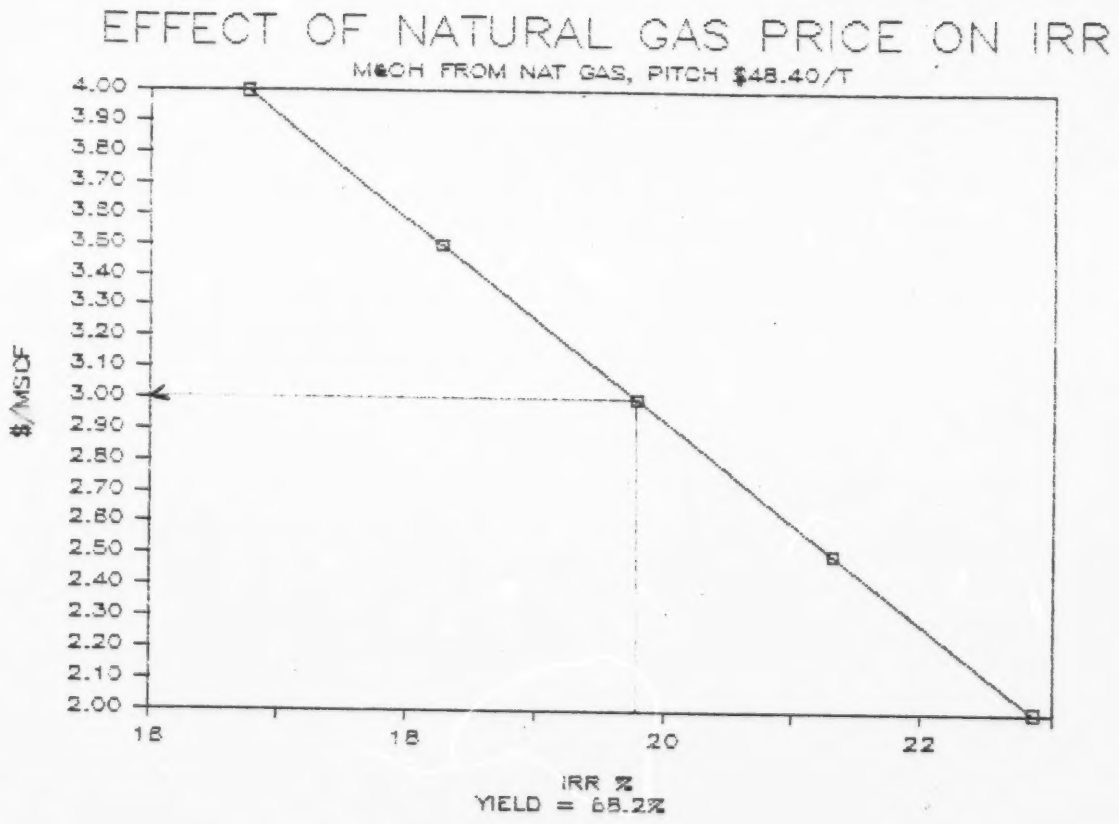

EFFECT OF NATURAL GAS PRICE ON IRR
MeOH FROM NAT GAS, PITCH $48.40/T
$/MSCF
4.00
3.90
3.80
3.70
3.60
3.50
3.40
3.30
3.20
3.10
3.00
2.90
2.80
2.70
2.60
2.50
2.40
2.30
2.20
2.10
2.00
16
18
20
22
IRR %
YIELD = 68.2%

Figure 23

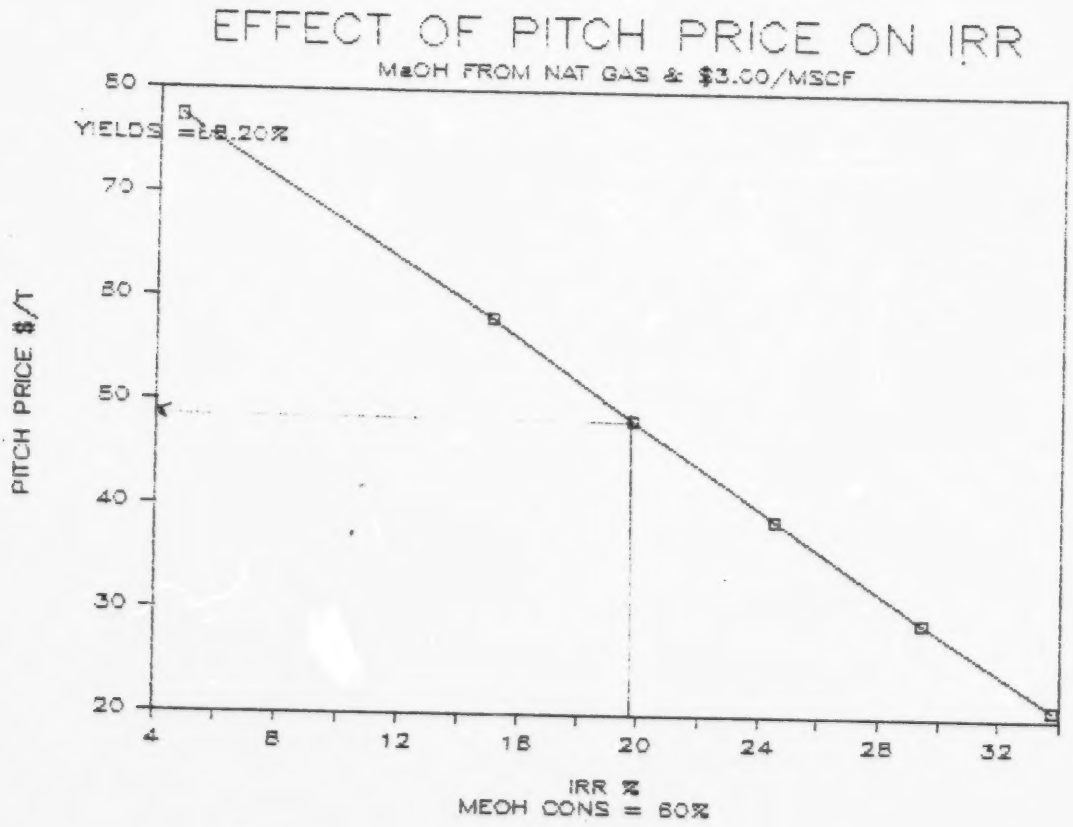

EFFECT OF PITCH PRICE ON IRR
MeOH FROM NAT GAS & $3.00/MSCF
YIELDS = 68.20%
PITCH PRICE $/T
60
70
80
50
40
30
20
4
8
12
16
20
24
28
32
IRR %
MEOH CONS = 60%

Figure 24

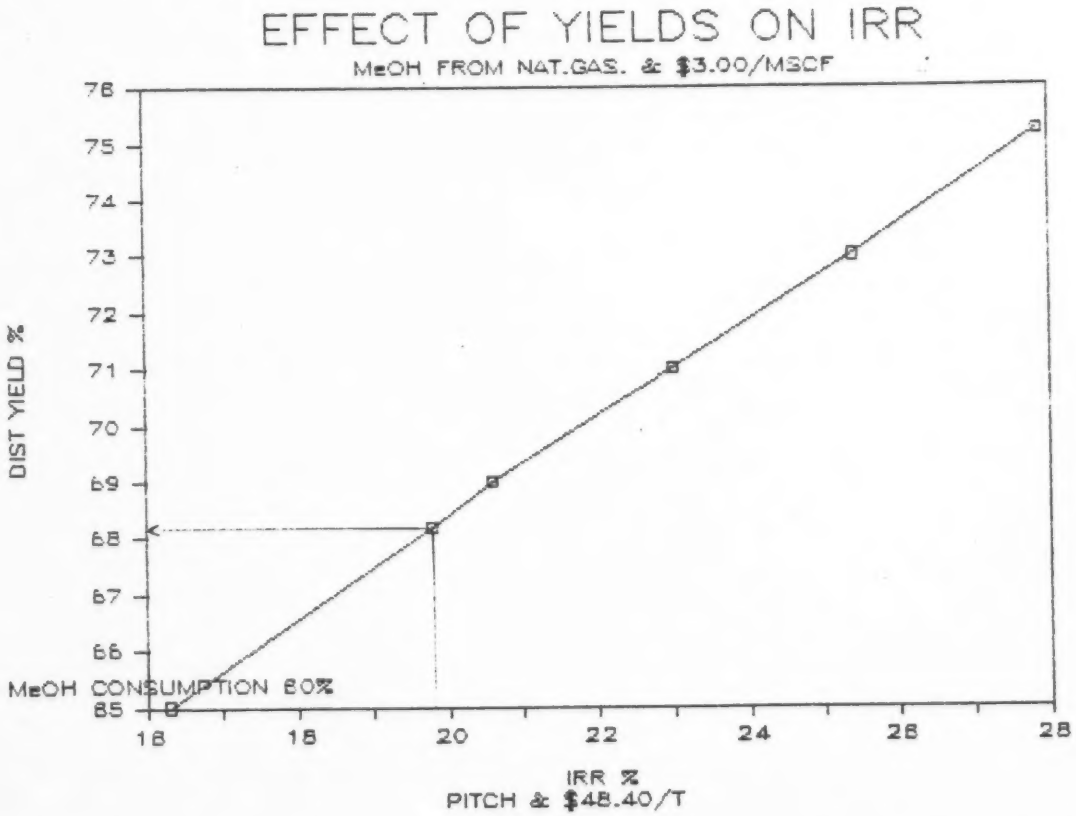
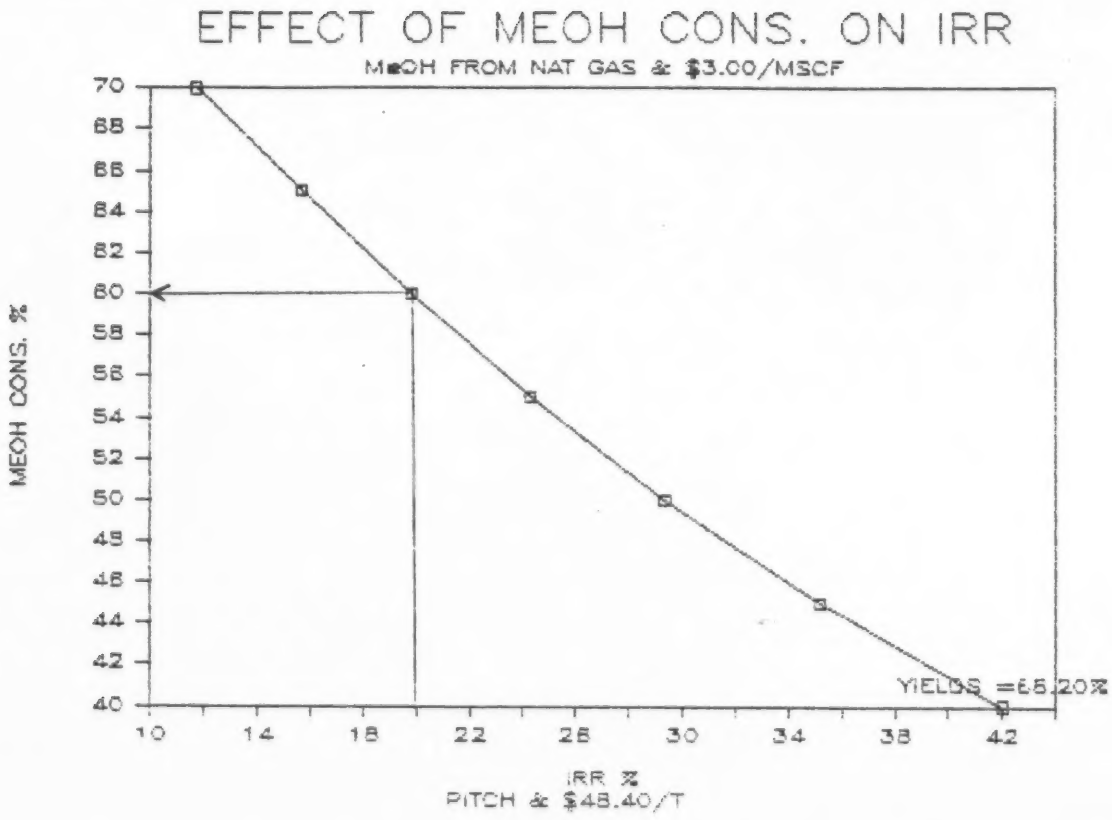

EFFECT OF YIELDS ON IRR
MeOH FROM NAT.GAS. & $3.00/MSCF
DIST YIELD %
78
75
74
73
72
71
70
69
68
67
66
65
MeOH CONSUMPTION 80%
16
18
20
22
24
26
28
IRR %
PITCH & $48.40/T

Figure 25


EFFECT OF MEOH CONS. ON IRR
MeOH FROM NAT GAS @ $3.00/MSCF
MEOH CONS. %
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
10
14
18
22
26
30
34
38
42
YIELDS =66.20%
IRR %
PITCH @ $48.40/T

APPENDIX A

ANALYTICAL PROCEDURES

ANALYTICAL PROCEDURES

Sampling Techniques

Generally, the materials handled such as: feed slurry, heavy product, light product and residue are heterogeneous. In order to obtain representative samples for analysis these materials must be thoroughly homogenized.

The sampling method employed is dependent on the nature of the sample at room temperature. Feed and heavy product were either heated to a liquid phase or cooled in the freezer and crushed with a mortar and pestle prior to mixing and sampling.

The light products are generally composed of two phases. These are separated into a aqueous fraction and an oil fraction and samples are taken of each for analysis.

METHODS OF ANALYSIS

Solvent Extraction

The products are considered to consist of solids, pre-asphaltenes, asphaltenes and oil. These are generally characterized by their solubility in different solvents.

In this report, solids are considered to be the fraction which is insoluble in tetrahydrofuran (THF) and consists of coke like material and catalyst; pre-asphaltenes are those that are soluble in THF but insoluble in toluene; asphaltenes are soluble in toluene but insoluble in n-heptane. The heptane soluble portion is considered to be oil.

The composition of each sample is determined by sequential extraction with solvents and then determining each fraction by difference as outlined earlier. Solvent extractions and insoluble collection is performed by vacuum filtration which allows for immediate analysis. Individual samples are used for each analysis.

For each analysis a sample is weighed in a beaker (approx. 1g) and dissolved by an excess (approx. 50 times the sample weight) of the appropriate solvent.

Maximum solvent extraction is accomplished by stirring the sample vigorously on a hot plate near the boiling point of the solvent for a minimum of thirty minutes.

The sample is allowed to cool to room temperature and then is filtered under vacuum using a preweighed glass fiber pad (whatman glass microfilter). The filter coke is washed with an excess amount of solvent and then dried in an oven until instant weight is achieved.

Vacuum Distillation

The apparatus used to carry out the distillation of the heavy product is shown schematically in Figure I. The distillation was done in two stages: 20-40mm Hg vacuum to remove a fraction distilling below 250 degree C, 0.2 to 1mm Hg vacuum to obtain all the other fractions: 250-350 degree C, 350 - 407 degree C, 407 - 450 degree C, 450 - 525 degree C, 525 degree C.

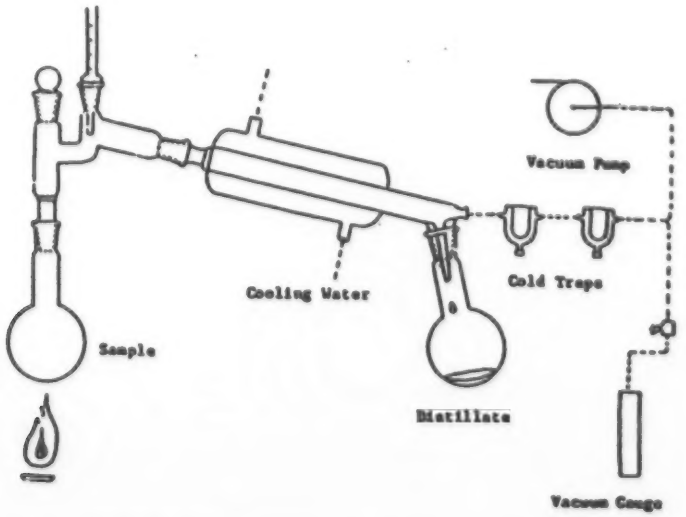
Procedure

Weigh 50-60gr of sample into the previously tared vacuum distillation flask. Seal the flask onto the apparatus using hi-temp-vac lubricant. Surround the traps with the proper coolant, start the vacuum and observe the flask content for signs of foaming. The pressure on the distillation assembly shall be lowered gradually to deaerate and minimize the foaming. When the equipment is air tight, apply a small flame into the flask. Adjust the burner so that the first drop of condensate will be collected after 10-15 minutes, at which point the temperature and pressure are noted and recorded. After the first fraction (250^{o}C) is collected, the distillation is stopped, the U-tube manometer replaced by the McLeod gauge and the water condenser is replaced by a vacuum connecting tube to prevent plugging line by the higher boiling fractions which tend to solidify at room temperature.

As soon as vapor or refluxing liquid appears at the joint between the flask and the column, adjust the rate of heating so that the distillation is recovered at a constant rate (approx. 2ml/min.). Continue the distillation until either the maximum temperature (525 degree C equivalent) is reached, or the cracking occurs (sudden rise in pressure or excessive smoking) in which case note the temperature at which cracking occurs.

After a distillation is completed, the apparatus should be allowed to cool for about 10 minutes before admitting air into it in order to prevent the possibility of vapor self-ignition. Use liquid nitrogen in the vacuum flask surrounding the glass trap.

FIGURE I



Simulated Distillation

The oil fraction recovered from the light products were characterized by simulated distillation as outlined in ASTM D-2887 to determine the boiling range distribution.

The simulated distillation system used consisted of Perkin Elmer Sigma 3 Gas Chromatograph with dual FID detectors and a sigma 10 data acquisition cansole.

The columns used were 61cm long, 0.32 cm. diameter. Stainless steel, packed with 10% SP 2100 on 60/80 supelcoport.

Column Temperature initial 60°C
final 330°C

Heating rate 8°C/min
Detector temperature 350°C
Inspector temperature 350°C
Carrier Nitrogen 30ml/min.

Calibration was accomplished with a mixture of n-paraffins from C_6 to C_{40}.

The boiling points were calculated at 10wt% intervals and include the initial and final boiling points which correspond to 0.5 and 99.5 wt% points.

Gas Chromatography:

The off gases were analysed for H_2, CO, CO_2, H_2S, CH_4, Dimethylether and C_2-C_5 hydrocarbons.

Two chromatographic systems were used; an automated AGE Carle Series SX which is comprised of an isothermal multi column gas chromatograph and a minigrator which is capable of collecting the data and controlling the GC operation and a Perkin Elmer Sigma 3B. equipped with a thermal conductivity detector and temperature programming.

Analysis of the Aqueous Phase

The aqueous phase of the light product is dilluted with isopropanol and analysed for methanol and water with a Perkin Elmer Sigma 3B Gas Chromatograph using a thermal conductivity detector. The column used is a 10 feet long, 1/8 inch diameter, stainless steel, packed with Chromosorb 102.

Column temperature - initial 120°C for 3 minutes
- final 175°C
- rate 15°C/min

Detector temperature 200°C
Injector temperature 300°C

It should be noted that when the oil phase is physically removed from the light product, the aqueous phase remains clouded as an emulsion. There will be additional separation of the oil from the aqueous phase as a function of time and physical conditions.

The amount of the oil remainings in the sample greatly affects the concentration of the "other compounds" and to a certain extent the concentration of methanol and water.

An attempt was done to check for the presence of some superior alcohols such as ethanol, isopropanol, propanol, isobutanol and butanol in the "other" category.

Pure compounds were injected in gas chromatograph equipped with a flame ionization detector.

The retention times of the pure compounds were checked against unknown peaks in the sample upon injection on two different columns. Chromosorb 102 and wide bore capillary column 5PB-1 stationary phase.

isopropanol, isobutanol and tertiary pentane seem to be present in some of the sample in concentration less than 1%.

Elemental Analysis

The elemental composition was determined using a Perkin Elmer 240 Elemental Analyzer with simultaneous analysis of Carbon, hydrogen and nitrogen as combustible matter.

Ash Determination

The ash content of the distillation residue was determined according to ASTM 3174-73.

Sulphur Determination

The total sulphur content of the distillation residue was determined as per ASTM D4239-9-83 using the Leco SC-32 sulphur analyser.

The SC-32 is an automatic direct reading instrument for the determination of total sulphur. The sample, weighing up to 0.5 g, is conbusted in oxygen in a resistance furnace at 1371.1 ^{0}C (2500 ^{0}F). The resulting SO_2 combustion product is selectively measured by solid state infrared detector. Detector output is weight compensate and displaced directly in percent sulphur.

APPENDIX B

PROPERTIES OF CATALYSTS

OF COMMERCIAL CATALYSTS

RED MUD (IRON OXIDE)

Supplier : Alcan

Composition : (Basis Wt.%)

$Fe2O_3$	33
TiO_2	6
SiO_2	17
Al_2O_3	20
CaO	1
Na_2O	9

H_2O (After Drying at Santech) 0.9

C 70 - 2 (Zinc/Chromium Oxide)

Supplier : United Catalysts Inc.

Nominal Content, (Wt%.)

ZnO	78
Cr_2O_3	22

AERO HDS - 1442A (Cobalt - Molybdena on Aluminum Base)

Supplier : American Cyanamid Company.

Composition, (Basis Wt.% dry basis)

MoO_3	13.2
CoO	3.5
Na_2O	0.03
SO_4	0.5
Fe	0.03

Physical Properties

Pore volume (H_2O), m^3/g	0.8
Surface area, m^2/g	300
Loss on ignition, wt.%	1.5

MOLYBDENUM HEXACARBONYL ($Mo(CO)_6$)

Supplier : Aldrich Company Co.

White powder, decomposing at 150°C without melting.

The ZSM-5 and MAP catalysts were supplied by the Scientific Authority and their composition was not communicated to Santech.

Cab-O-Sil (Fumed Silica)

Supplier : Cabot Carbon of Canada

Grade : M S-7

Composition, (Wt%)

Silica	99.8

Physical Properties

Nominal Particle diameter ( )		0.014
Surface Area	(m^2/g)	200 25
Density	(Kg/m^3)	72 8

Method of Manufacture

Cab-O-Sil in produced by the hydrolysis of silica tetrachloride vapour in a flame of hydrogen and oxygen. In the process, molten spheres, termed primary particles, collide and fuse with one another to form branched, three-dimensional, chain-like aggregates.